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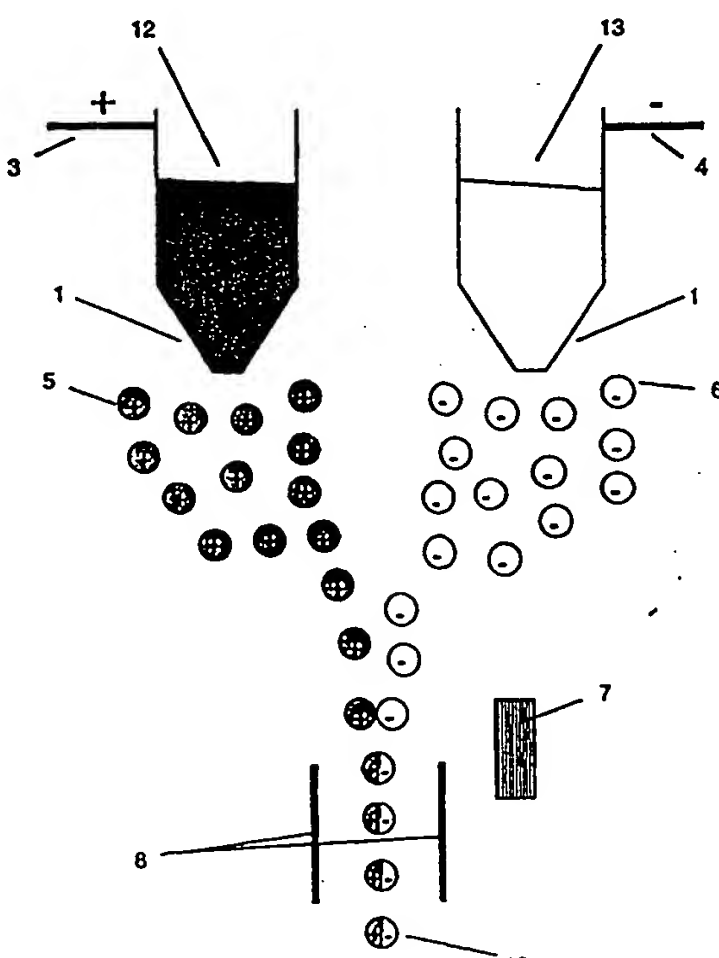
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 6 :</b> G02F 1/133, B41J 2/01, B29C 67/00, G09F 9/00, G04B 47/00, G09F 9/37	<b>A1</b>	<b>(11) International Publication Number:</b> WO 98/03896 <b>(43) International Publication Date:</b> 29 January 1998 (29.01.98)
<b>(21) International Application Number:</b> PCT/US96/13469 <b>(22) International Filing Date:</b> 20 August 1996 (20.08.96)  <b>(30) Priority Data:</b> 60/022,222 19 July 1996 (19.07.96) US  <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US 60/022,222 (CIP) Filed on 19 July 1996 (19.07.96)  <b>(71)(72) Applicant and Inventor:</b> JACOBSON, Joseph, M. [US/US]; Apartment 1, 31 Linnaean Street, Cambridge, MA 02138 (US).  <b>(74) Agents:</b> SMITH, James, M. et al.; Hamilton, Brook, Smith & Reynolds, Two Militia Drive, Lexington, MA 02173 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ELECTRONICALLY ADDRESSABLE MICROENCAPSULATED INK AND DISPLAY THEREOF  <b>(57) Abstract</b> <p>We describe a system of electronically active inks which may include electronically addressable contrast media, conductors, insulators, resistors, semiconductive materials, magnetic materials or spin materials. We further describe a printing system capable of laying down said materials in a definite pattern. Such a system may be used for instance to print a flat panel display complete with onboard drive logic or to print a working logic circuit onto any of a large class of substrates.</p> 		

-1-

ELECTRONICALLY ADDRESSABLE MICROENCAPSULATED INK  
AND DISPLAY THEREOF

Related Applications

This application claims priority to U.S. Provisional  
5 Application Serial No. 60/022,222, filed July 19, 1996 the  
contents of which are incorporated herein by reference in  
their entirety.

Background

Currently printing of conductors and resistors is  
10 well known in the art of circuit board manufacture. In  
order to incorporate logic elements the standard practice  
is to surface mount semiconductor chips onto said circuit  
board. To date there does not exist a system for directly  
printing said logic elements onto an arbitrary substrate.

15 In the area of flat panel display drivers there  
exists technology for laying down logic elements onto  
glass by means of vacuum depositing silicon or other  
semiconductive material and subsequently etching circuits  
and logic elements. Such a technology is not amenable to  
20 laying down logic elements onto arbitrary surface due to  
the presence of the vacuum requirement and the etch step.

In the area of electronically addressable contrast  
media as may be used to effect a flat panel display  
emissive and reflective electronically active films such  
25 as electroluminescent and electrochromic films, polymer,  
dispersed liquid crystal films, and bichromal microsphere  
elastomeric slabs are known. No such directly  
electronically addressable contrast media however is  
amenable to printing onto an arbitrary surface.

-3-

In another embodiment this invention provides for a semiconductive ink system in which a semiconductor material is deployed in a binder such that when said binder is cured a percolated structure with semiconductive  
5 ~~properties results.~~

In another embodiment this invention for provides for systems capable of printing an arbitrary pattern of metal or semiconductive materials by means of photoreduction of a salt, electron beam reduction of a salt, jet  
10 electroplating, dual jet electroless plating or inert gas or local vacuum thermal, sputtering or electron beam deposition.

In another embodiment this invention provides for semiconductor logic elements and electro-optical elements  
15 which may include diode, transistor, light emitting, light sensing or solar cell elements which are fabricated by means of a printing process or which employ an electronically active ink system as described in the aforementioned embodiments. Additionally said elements  
20 may be multilayered and may form multilayer logic including vias and three dimensional interconnects.

In another embodiment this invention provides for an electronically addressable display in which some or all of address lines, electronically addressable contrast media,  
25 logic or power are fabricated by means of a printing process or which employ an electronically active ink system as described in the aforementioned embodiments.

In another embodiment this invention provides for an electrostatic actuator or motor which may be in the form  
30 of a clock or watch in which some or all of address lines, logic or power are fabricated by means of a printing process or which employ an electronically active ink system as described in the aforementioned embodiments.

-5-

Figure 4A-M are schematic representations of microencapsulated electronically addressable contrast media systems suitable for bottom addressing.

Figures 5A-D are schematic representations of  
5 microencapsulated electronically addressable contrast media systems based on a dielectrophoretic effect.

Figures 6A-B are schematic representations of microencapsulated electronically addressable contrast media systems based on a frequency dependent  
10 dielectrophoretic effect.

Figures 6C-E are plots of the dielectric parameter as a function of frequency for various physical systems.

Figures 7A-D are schematic representations of electronic ink systems and means for printing the same.

15 Figure 8 is a schematic representation of a laser reduced metal salt ink system.

Figures 9A-E are schematic representations of electronic ink systems and means for printing the same.

Figures 10A-D are schematic diagrams of printed  
20 transistor structures.

Figure 11 is a schematic diagram of an electronic display employing printed elements.

Figure 12 is a schematic diagram of an electrostatic motor which may be in the form of a watch or clock in  
25 which said electrostatic elements are printed

Figure 13 is a schematic diagram of a watch in which the wristband of said watch incorporates an electronically addressable display having printed elements.

Figure 14 is a schematic diagram of a spin computer.

30 Detailed Description of a Preferred Embodiment

Means are known in the prior art for producing

-7-

time as is known in the art of electrets. A heating element 7 may serve to reheat said pair thus minimizing surface tension energy and serving to reform said pair into a more perfect spherical shape. Finally a set of  
5 electrodes 8 biased at either the same or opposite voltage may be employed to trap particles which are not overall charge neutral.

Referring to Figure 1B a similar apparatus may be employed to create a monochromal particle with an  
10 implanted dipole. In this arrangement nozzles containing material of the same color 12 are employed as before to create a monochromal particle with implanted dipole 21.

Referring to Figure 1C and E alternative means are shown for producing a bichromal particle with implanted  
15 dipole by means of combining two differentially colored materials 12 and 13 on a spinning disk 11 or in a double barreled nozzle 19. Said materials are charged by means of positive electrode 14 and negative electrode 15 and combine by means of electrostatic attraction at the rim of  
20 said disk or exit of said double barrel nozzle to form bichromal particle with implanted dipole moment 16. Said means differs from that known in the art by means of causing said two different materials 12 and 13 to coalesce by means of electrostatic attraction as opposed to relying  
25 on surface properties and interactions between the two materials. Additionally the present scheme creates a particle with an implanted dipole moment 16 which may serve to create a large dipole moment than that possible from the naturally occurring Zeta potential.

30 Referring to Figure 1D and F a similar apparatus may be employed to create a monochromal particle with an implanted dipole. In this arrangement nozzles containing material of the same color 12 are employed as before to

-9-

An alternate means of microencapsulation is shown in Figure 2C. In this scheme a light source 82 which may be a UV light source passes in some areas through a photomask 84 exposing a crosslinkable polymer which may be caused to  
5 form a cellular structure 86. The individual cells of said cellular structure may then be filled with an internal phase 25.

Employing the systems described in Figures 2A-C it is possible to microencapsulate systems with electronically  
10 active properties specifically electronically addressable contrast media. Figure 3 details such electronically addressable contrast media systems which are suitable for addressing by means of a top clear electrode 100 and bottom electrode 110. Referring to Figure 3A a  
15 microcapsule 120 may contain a microsphere with a positively charged hemisphere 142 and a negatively charged 140 hemisphere and an associated surface layer material 130. If said hemispheres are differentially colored an electric field applied to said electrodes may act to  
20 change the orientation of said sphere thus causing a perceived change in color.

Referring to Figure 3B a microcapsule 120 may contain positively charged particles of one color 210 and negatively charged particles of another color 220 such  
25 that application of an electric field to said electrodes causes a migration of the one color or the other color, depending on the polarity of the field, toward the surface of said microcapsule and thus effecting a perceived color change. Such a system constitutes a microencapsulated  
30 electrophoretic system.

Referring to Figures 3C-D a microcapsule 120 may contain a dye, dye precursor or dye indicator material of a given charge polarity 230 or a dye, dye precursor or dye

-11-

Referring to Figures 4A-M it may be desirable to develop ink systems which are suitable for use without a top transparent electrode 100 which may degrade the optical characteristics of the device. Referring to

5 Figures 4A and B the chemistry as described in reference to Figures 3C-D may be employed with in-plane electrodes such that said chemistry undergoes a color switch from one color state to a second color state upon application of an electric field to in-plane electrodes 270 and 280. Such a

10 system is viewed from above and thus said electrodes may be opaque and do not effect the optical characteristics of said display.

As another system in-plane switching techniques have been employed in transmissive LCD displays for another

15 purpose, namely to increase viewing angle of such displays. Referring to Figures 4C and 4D a bistable liquid crystal system of the type demonstrated by Hatano et. al. of Minolta Corp. is modified to be effected by in plane electrodes such that a liquid crystal mixture

20 transforms from a first transparent planar structure 290 to a second scattering focal conic structure 292.

Referring to Figure 4E the system of Figure 3E may be switched by use of in-plane electrodes 270 and 280.

Other systems may be created which cause a first

25 color change by means of applying an AC field and a second color change by means of application of either a DC field or an AC field of another frequency. Referring to Figures 4F-G a hairpin shaped molecule or spring in the closed state 284 may have attached to it a positively charged 282

30 and a negatively charged 283 head which may be microspheres with implanted dipoles. Additionally one side of said hairpin shaped molecule or spring has attached to it a leuco dye 286 and the other side of said



-13-

Referring to Figure 4L and M a similar system is possible but instead of a polymer leuco and reducing groups may be attached to oppositely charge microspheres directly by means of a bridge 296 which may be a  
5 biotin-streptavidin bridge, polymer bridge or any other suitable bridge. As before application of a DC field cause leuco and reducing groups to become distal whereas application of a reverse DC field or AC field brings into random contact the leuco and reducing groups. A polymer  
10 may be added to aid in the stability of the oxidized state.

Referring to Figures 5A-D and Figures 6A-B an entirely different principle may be employed in an electronically addressable contrast media ink. In these  
15 systems the dielectrophoretic effect is employed in which a species of higher dielectric constant may be caused to move to a region of high electric field strength.

Referring to Figures 5A and 5B a non-colored dye solvent complex 315 which is stable when no field is  
20 applied across electrode pair 150 may be caused to become dissociate into colored dye 300 and solvent 310 components by means of an electric field 170 acting differentially on the dielectric constant of said dye complex and said solvent complex as applied by electrode pair 150. It is  
25 understood that the chemistries as discussed in the system of Figures 3C-D may readily be employed here and that said dye complex and said solvent complex need not themselves have substantially different dielectric constants but rather may be associated with other molecules or particles  
30 such as microspheres with substantially different dielectric constants. Finally it is understood that a gel or polymer complex may be added to the contents of said microcapsule in order to effect a bistability.

-15-

field region proximal the electrodes thus displacing material 182 and thus causing said microcapsule to appear as the color W when viewed from above. If B and W correspond to Black and White then a black and white display may be effected. A polymer material may be added to internal phase 184 to cause said system to be bistable in the field off condition. Alternatively stiction to the internal side wall of said capsule may cause bistability.

Referring to Figure 6A, material 182 and Figure 6C, this patent teaches the fabrication of a particle with an engineered frequency dependent dielectric constant. The means for fabricating this particle are depicted in Figures 1B, E and F. At low frequency such dipolar particles have sufficiently small mass that they may rotate in phase with said AC field thus effectively canceling said field and acting as a high dielectric constant material. At high frequency however the inertia of said particles is such that they cannot keep in phase with said AC field and thus fail to cancel said field and consequently have an effectively small dielectric constant.

Alternatively material 182 may be comprised of naturally occurring frequency dependent dielectric materials. Materials which obey a frequency dependence functionality similar to the artificially created dipole material discussed above and which follow curves similar to Figure 6C, curve 322 include materials such as Hevea rubber compound which has a dielectric constant of  $K = 36$  at  $f = 10^3$  Hz and  $K = 9$  at  $f = 10^6$  Hz, materials with ohmic loss as are known in Electromechanics of Particles by T.B. Jones incorporated herein by reference and macromolecules with permanent dipole moments.

Additionally material 182 may be a natural or

-17-

proximal to said electrodes thus causing said microcapsule to appear as a mixture of the colors C and M when viewed from above. Finally if an AC field of frequency  $f_3$  is applied by means of electrodes 270 and 280 internal phase  
5 190 of color C will be attracted to the high field region proximal to said electrodes thus causing said microcapsule to appear as a mixture of the colors M and Y when viewed from above. If C M and Y correspond to Cyan, Magenta and Yellow a color display may be effected.

10 It is understood that many other combinations of particles with frequency dependent dielectric constants arising from the physical processes discussed above may be employed to effect a frequency dependent electronically addressable display.

15 In addition to the microencapsulated electronically addressable contrast media ink discussed in Figures 3-6, figures 7-9 depict other types of electronically active ink systems. In the prior art means are known for depositing metals or resistive materials in a binding  
20 medium which may later be cured to form conducting or resistive traces. In the following description novel means are described for depositing semiconductive materials in a binder on a large class of substrate materials in one case and for depositing metals, resistive  
25 materials or semiconductive materials outside of vacuum, in an arbitrary pattern, without the need for an etch step and on a large class of substrate materials in another case.

In one system a semiconductor ink 350 may be  
30 fabricated by dispersing a semiconductor powder 355 in a suitable binder 356. Said semiconductive powder may be Si, Germanium or GaAs or other suitable semiconductor and may further be with n-type impurities such as phosphorous,

-19-

As an example, to form a metallic trace Silver Nitrate (AgNO<sub>3</sub>) may be used for jet 420 and a suitable aldehyde may be used for the reducing jet 430. Many other examples of chemistries suitable for the present system are known  
5 in the art of electroless plating. In all such examples it is understood that said jets are moveable and controllable such that an arbitrary trace may be printed.

Referring to Figure 9B a system which is similar to that of Figure 9A is depicted. In this case an electron  
10 beam 470 may be used instead of said reducing jet in order to bring about a reduction of a metal or semiconductive salt emanating from a jet 460. A ground plane 450 may be employed to ground said electron beam.

Referring to Figure 9C an ink jet system for  
15 depositing a metallic or semiconductive trace is depicted based on electroplating. In this system a metal or semiconductive salt in a jet 480 held at a potential V may be electroplated onto a substrate 410 thus forming a metallic or semiconductive trace.

20 Referring to Figure 9D means are known in the prior art for UV reduction of a metal salt from an ink jet head. In the present system a jet containing a metal or semiconductive salt 490 may be incident upon a substrate 400 in conjunction with a directed light beam 495 such  
25 that said metal or semiconductive salt is reduced into a conductive or semiconductive trace 410. Alternatively jet 490 may contain a photoconductive material and a metal salt which may be caused to be photoconductively electroplated onto surface 400 by means of application of  
30 light source 495 as is known in the field of photoconductive electroplating.

Referring to Figure 9E a system is depicted for a moveable deposition head 500 which contains a chamber 520

-21-

The ink systems and printing means discussed in the foregoing descriptions may be useful for the fabrication of a large class of electronically functional structures. Figures 11-14 depict a number of possible such structures  
5 which may be fabricated.

Referring to Figure 11, an electronic display, similar to one described in a copending patent by Jacobson, is comprised of electronically addressable contrast media 640, address lines 610 and 620 and logic  
10 elements 670 all or some of which may be fabricated with the ink systems and printing means as described in the foregoing descriptions.

Referring to Figure 12 an electrostatic motor which may form an analog clock or watch is depicted which  
15 consists of printed conducting elements 720, 730, 740 and 760 which are printed onto substrate 700. Said elements, when caused to alternately switch between positive negative or neutral states by means of a logic control circuit 710 may cause an element 750 to be translated thus  
20 forming a motor or actuator. In the device of Figure 12 some or all of said conducting elements and/or logic control elements may be printed using the ink systems and printing means described in the foregoing description.

Referring to Figure 13 a wrist watch 800 is depicted  
25 in which the band 820 of said watch contains an electronically addressable display 830 in which some or all of the components of said display, including the electronically addressable contrast media, the address lines and/or the logic are fabricated by means of the ink  
30 systems and printing means described in the foregoing description. Such a fabrication may be useful in terms of producing and inexpensive, easily manufacturable and thin display function. Control buttons 810 may serve to

-23-

CLAIMS

What is claimed is:

1. An electronically active ink comprising a microencapsulated system having an optical reflectance which may be modulated by means of application of an electric field.  
5
2. The ink of claim 1 in which said microencapsulated system is suitable for addressing by means of top and bottom electrodes.
- 10 3. The ink of claim 1 in which said microencapsulated system is suitable for addressing solely by means of bottom electrodes.
4. The ink of claim 1 in which said microencapsulated system is suitable for addressing by means of an AC electric field which may be modulated at a first frequency to effect a first optical reflectance and at a second frequency to effect a second optical reflectance.  
15
5. The ink of claim 4 in which said modulatable optical reflectances correspond to modulatable colors.  
20
6. Means of fabricating a bichromal particle employing electrostatically charged atomizers.
7. Means of fabricating a bichromal particle in which differentially colored materials are electrostatically attracted to each other on a  
25

-25-

15. The ink of claim 1 in which said microencapsulated system is based on a dielectrophoretic effect.
16. An electronic display in which display elements employ a frequency dependent dielectrophoretic effect in which an AC electric field modulated at a first frequency effects a first optical reflectance and an AC electric field modulated at a second frequency effects a second optical reflectance.
17. The ink of claim 15 in which said dielectrophoretic effect is a frequency dependent dielectrophoretic effect.
18. The ink of claim 17 in which said frequency dependence is due to a particle with an implanted dipole.
19. The ink of claim 17 in which said frequency dependence is due to an elastomeric, ohmic loss, artificial or natural cell structure or natural dipole.
20. The ink of claim 18 in which said particle is fabricated by means of electrostatically charged atomizers, spinning disk or double barrel nozzle.
21. The ink of claim 1 in which said microencapsulated system is based on a two part dye and solvent or reducing and oxidizing system.
22. An electronic display in which display elements are comprised of a dye which is associated with a head of

-27-

system is based on an electroluminescent system coupled to an electronically active dye system.

29. The ink of claim 1 in which said microencapsulated system is based on a bistable liquid crystal system.
- 5 30. The ink of claim 1 in which said microencapsulated system is individually microencapsulated.
31. The ink of claim 1 in which said microencapsulated system is matrix microencapsulated.
- 10 32. An electronically active ink comprising a microencapsulated spin system.
33. An electronically active ink comprised of a semiconductive material in a binder.
- 15 34. A printing means for printing a conducting or semiconducting trace by means of causing a light source to be scanned such that a substrate containing a microencapsulated salt is reduced and burst in areas where said light source impinges thus forming said conducting or semiconducting trace.
- 20 35. A printing means for printing a conducting or semiconducting trace by means of moveable jets in which one such jet contains a salt and another such jet contains a reducing agent.
- 25 36. A printing means for printing a conducting or semiconducting trace by means of a moveable jet and electron beam in which a salt from said jet is



-29-

44. An electrostatic motor or actuator in which some or all of address lines, logic or power elements are fabricated by means of a printing process.
- 5 45. A wristwatch band comprising an electronically addressable display in which some or all of address lines, electronically addressable contrast media, logic or power elements are fabricated by means of a printing process.
- 10 46. A wristwatch band comprising an electronically addressable display in which some or all of address lines, electronically addressable contrast media, logic or power elements employ an electronically active ink.
- 15 47. A spin computer in which some or all of address lines, electronically addressable spin media, logic or power elements are fabricated by means of a printing process.
- 20 48. A spin computer in which some or all of address lines, electronically addressable spin media, logic or power elements employ an electronically active ink.

1/25

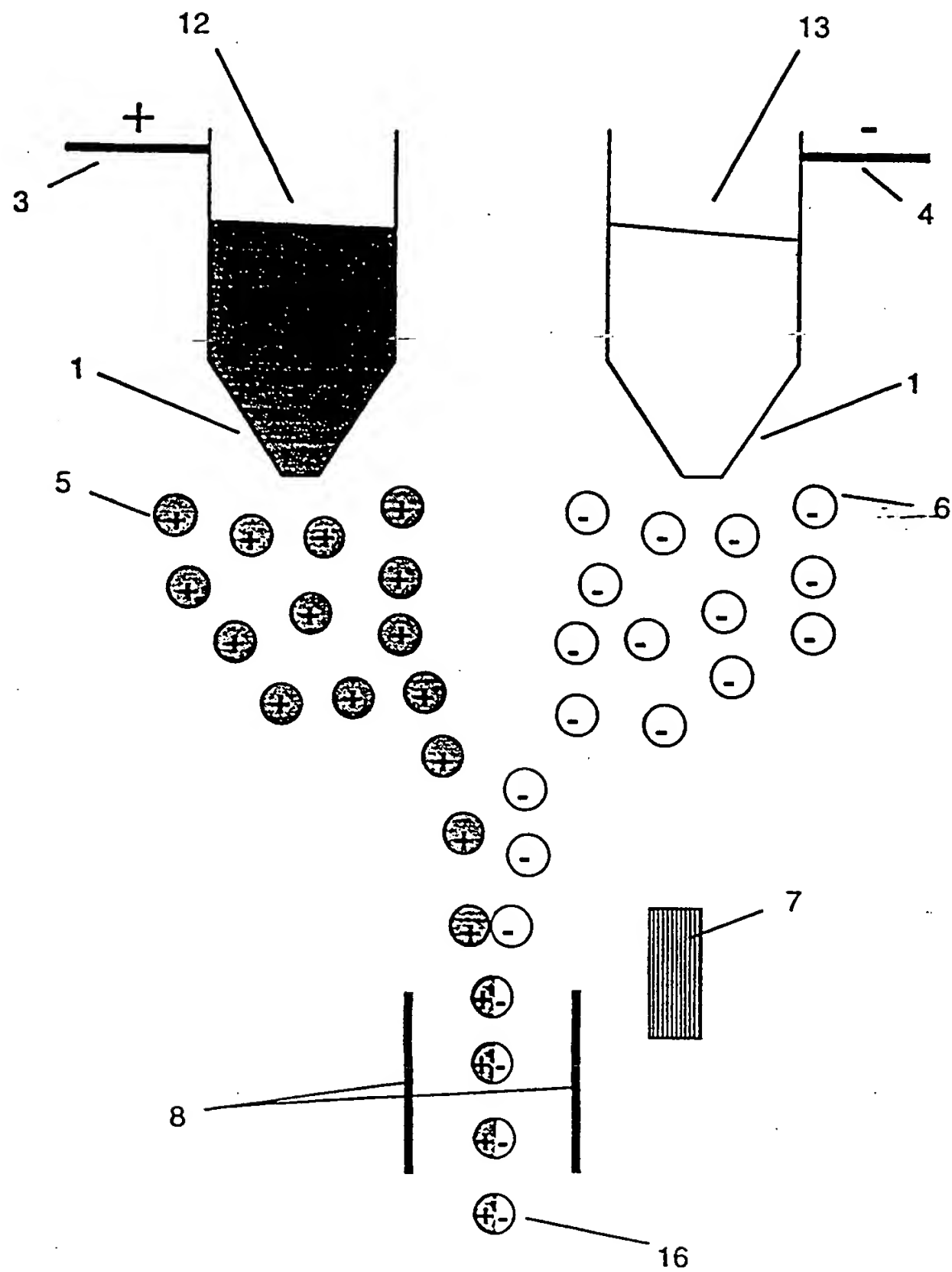


FIG 1 A

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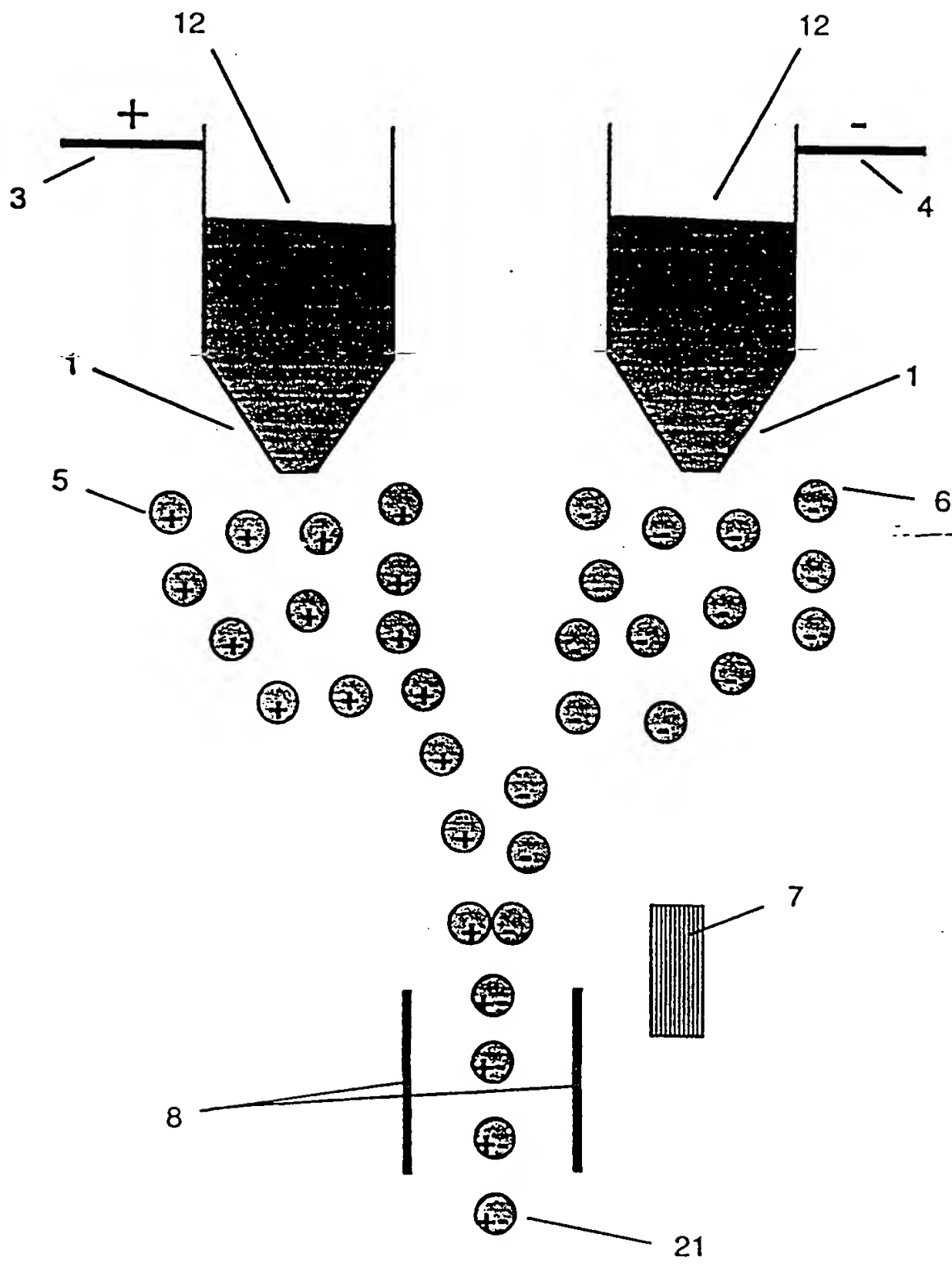


FIG 1 B

3/25

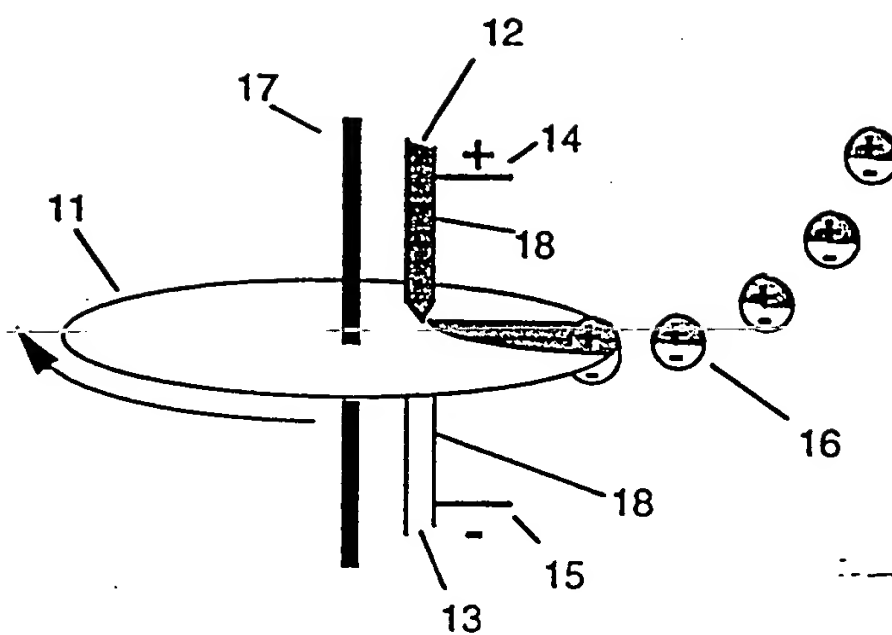


FIG 1 C

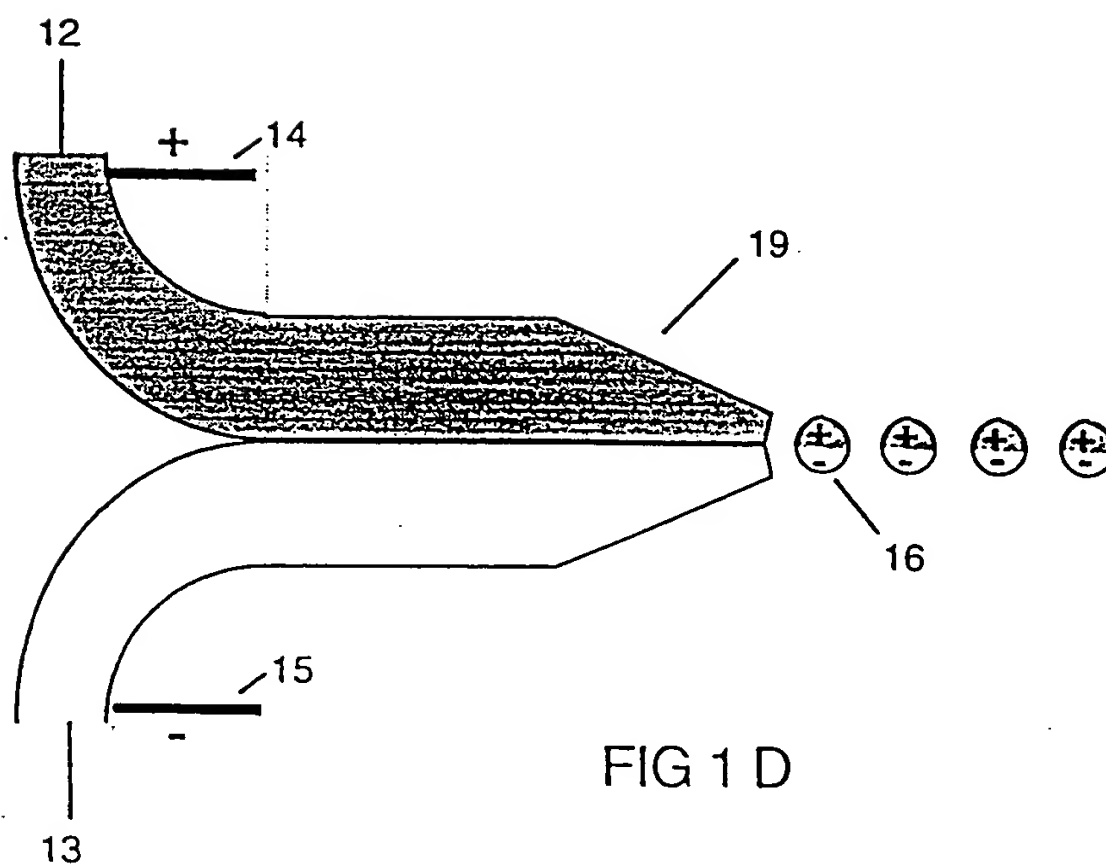


FIG 1 D

4/25

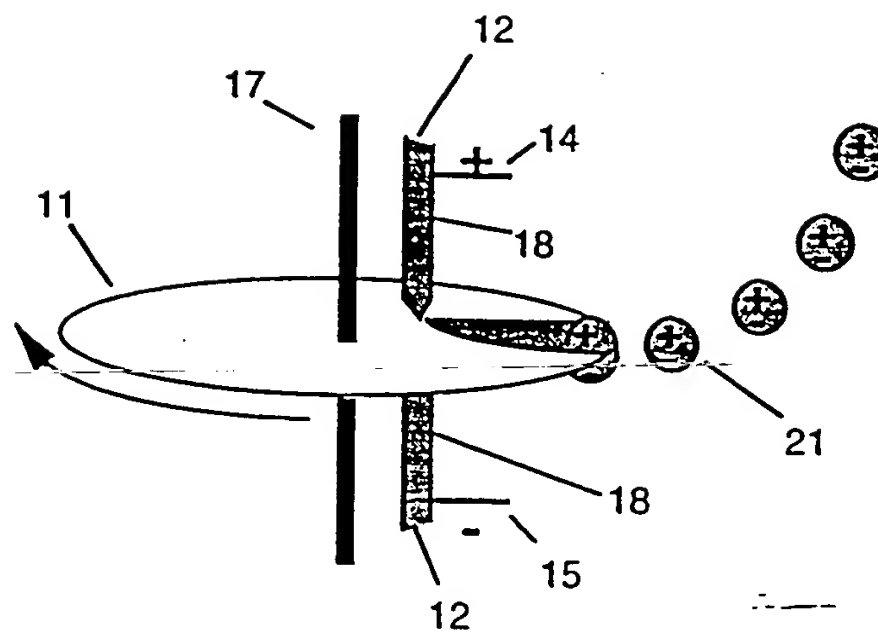


FIG 1 E

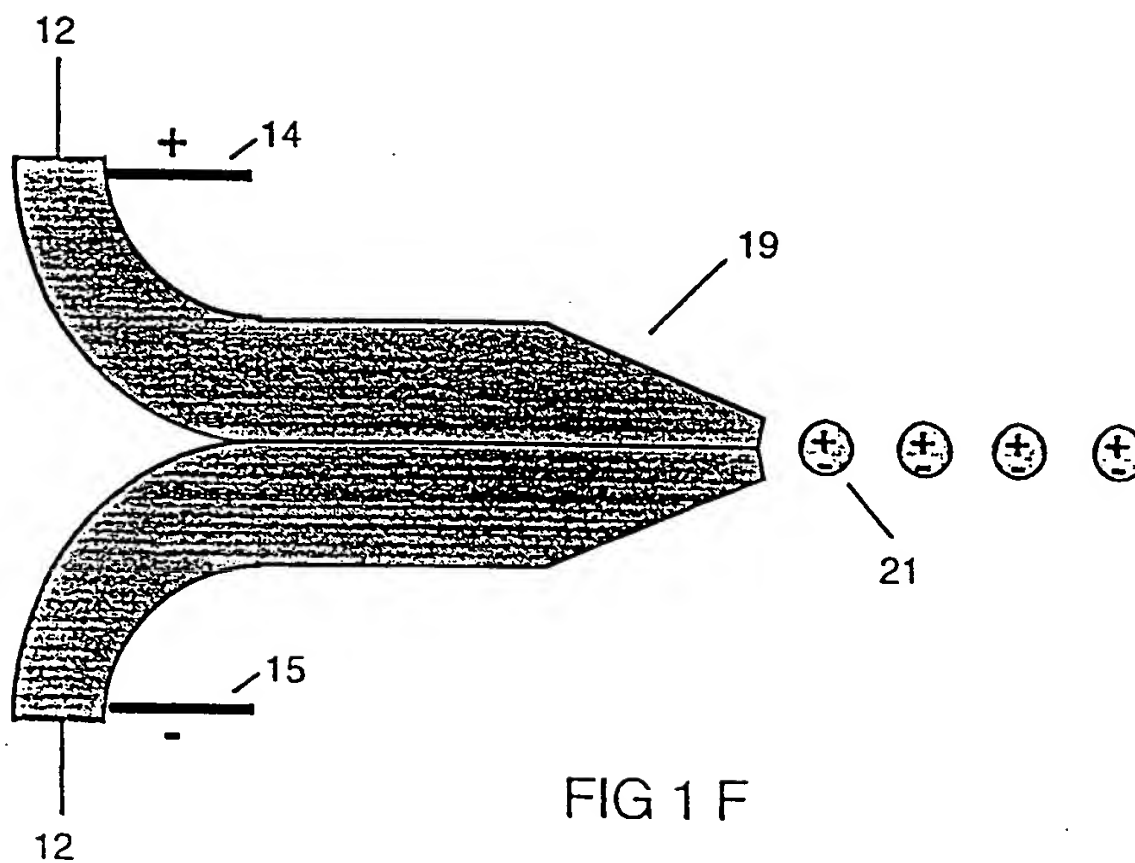


FIG 1 F

5/25

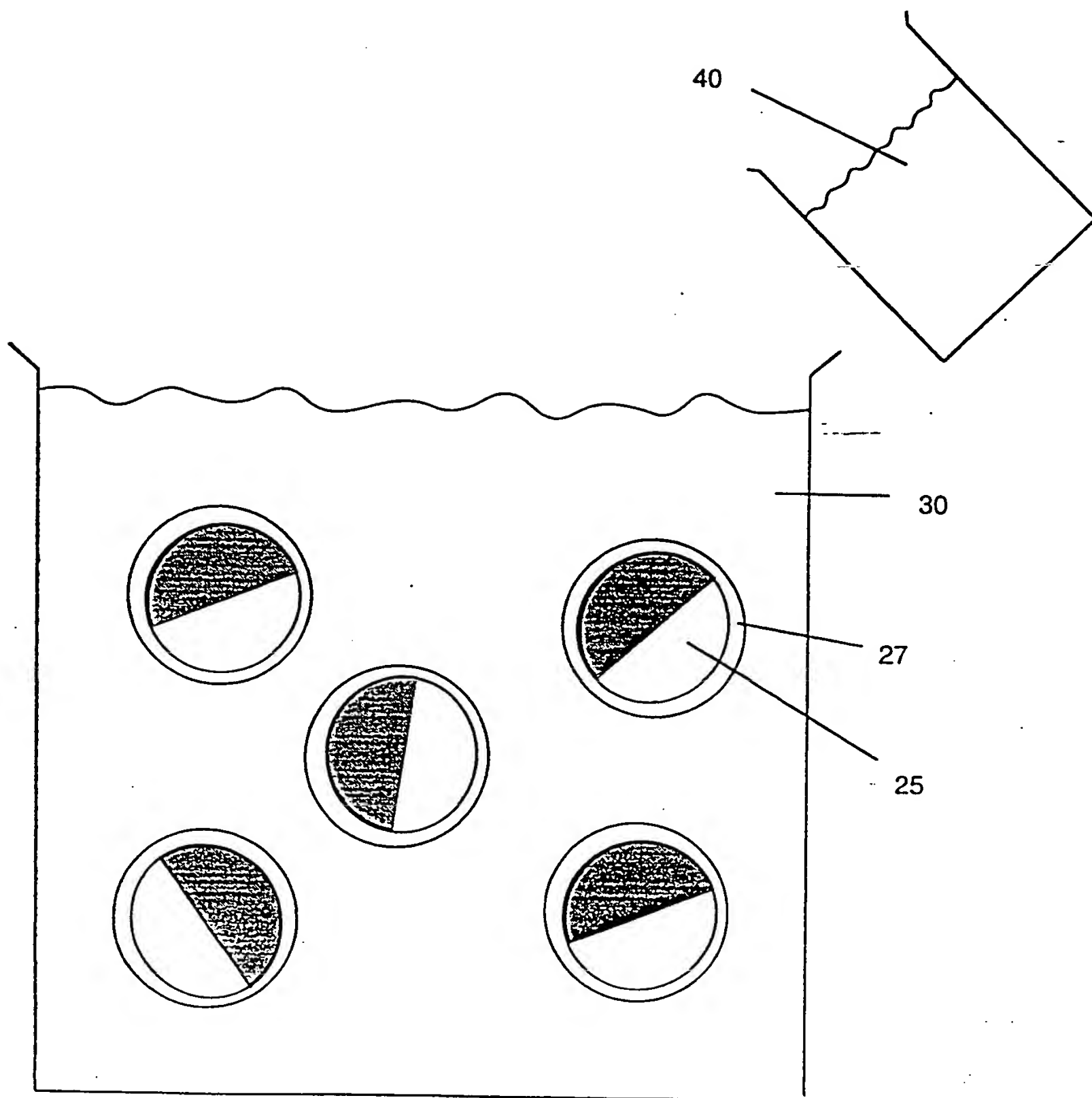


FIG 2 A

6/25

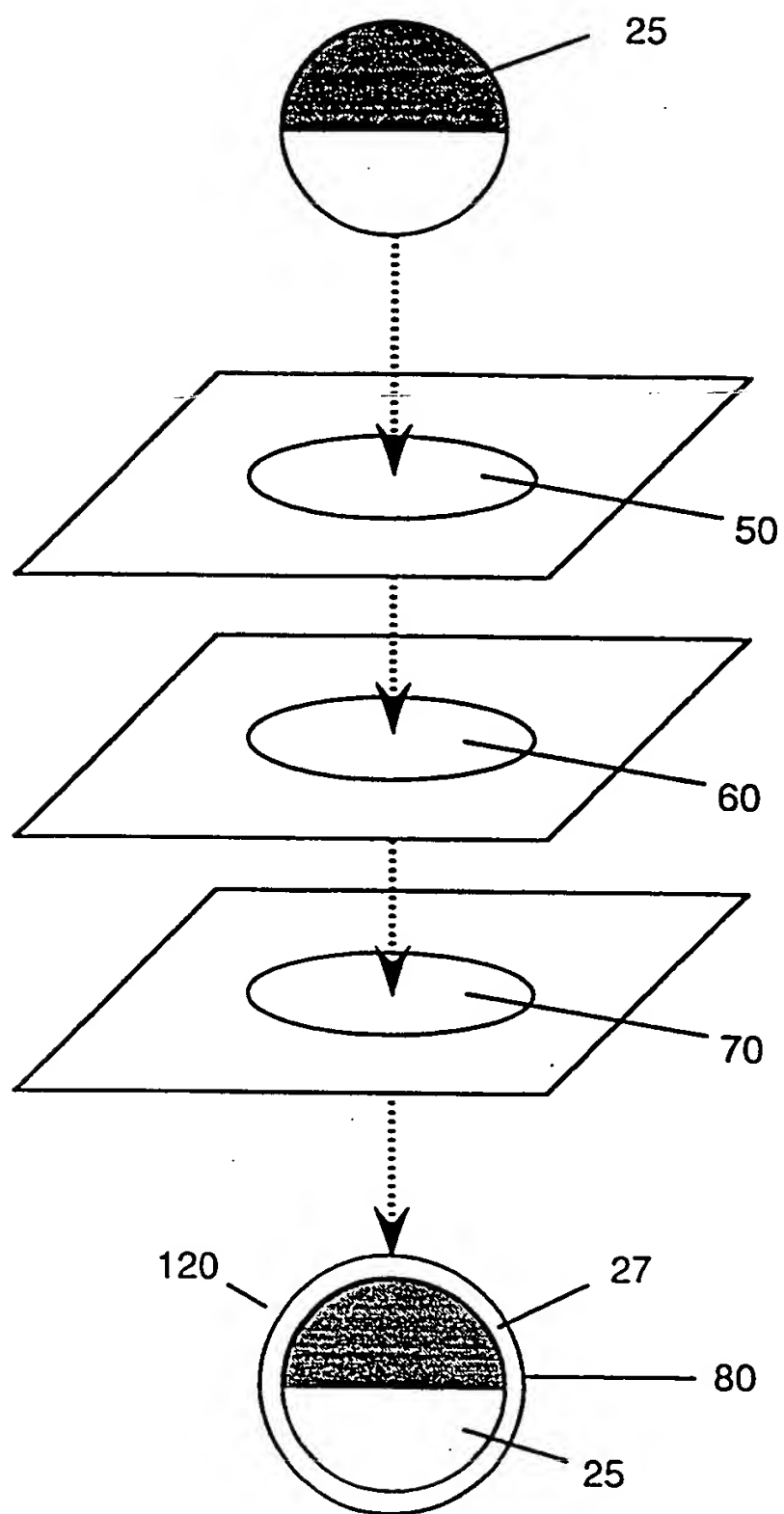


FIG 2 B

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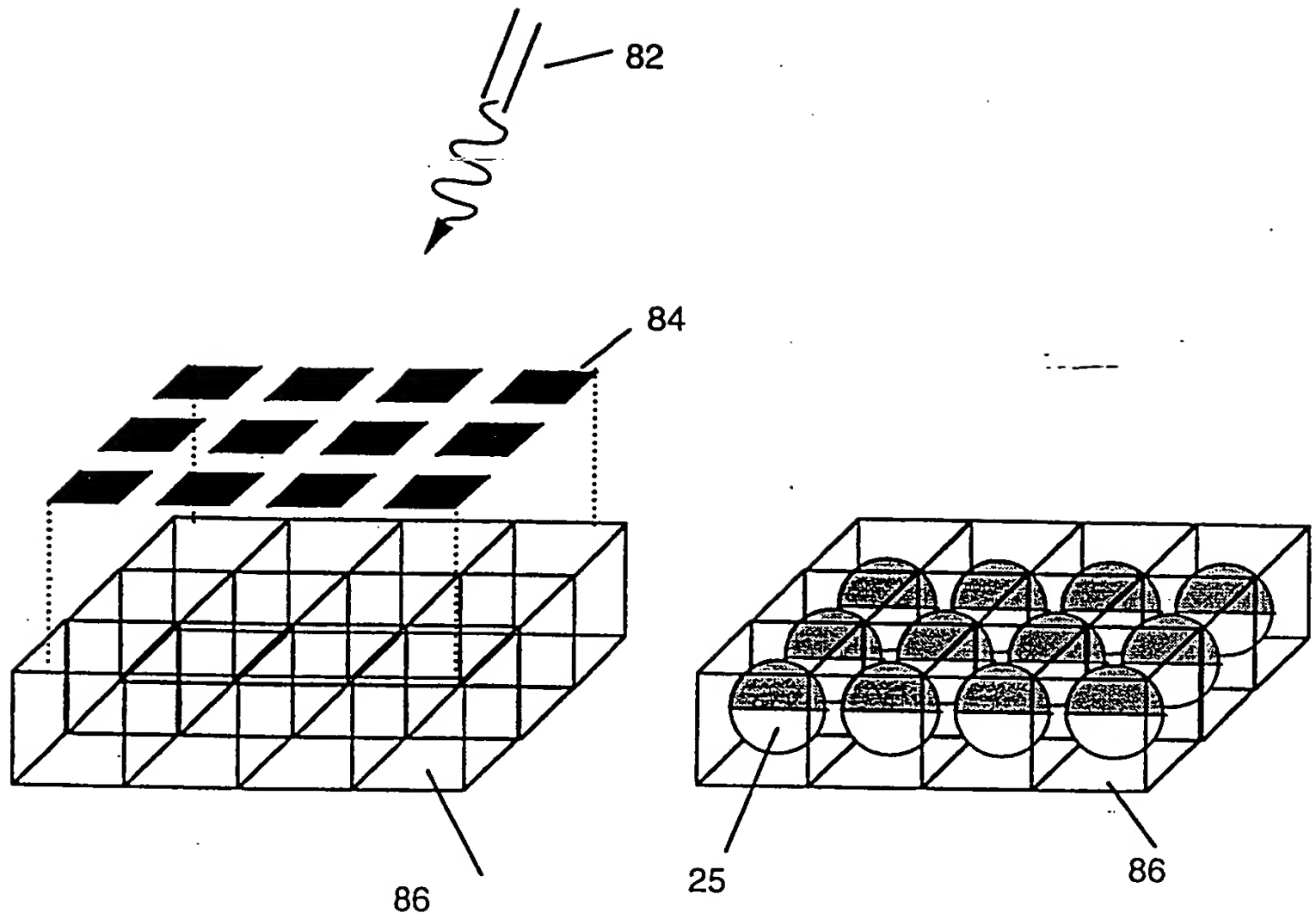
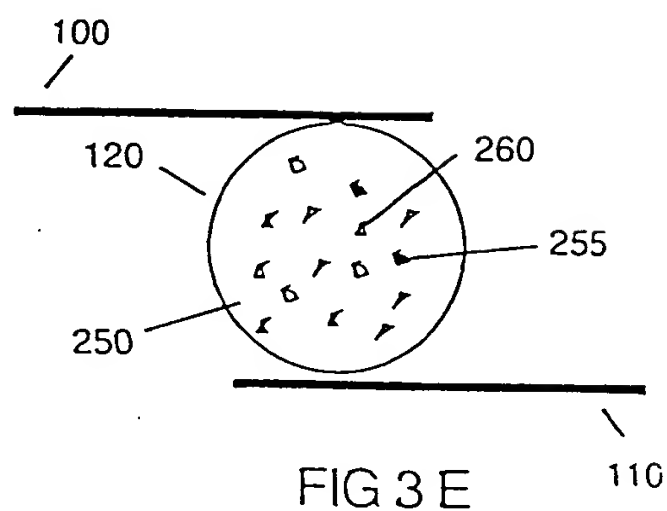
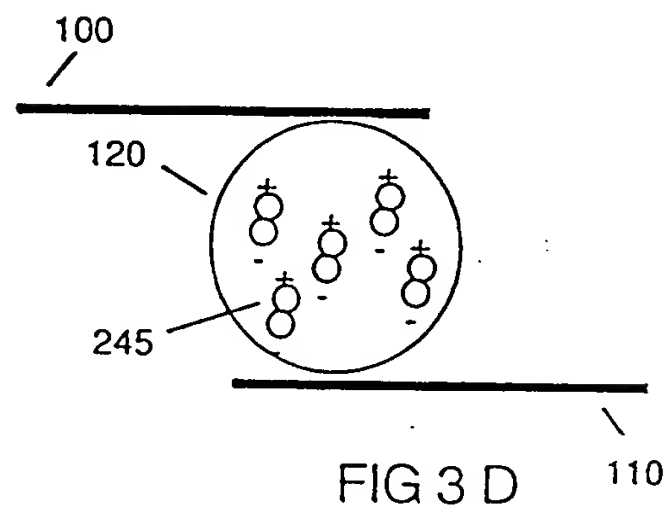
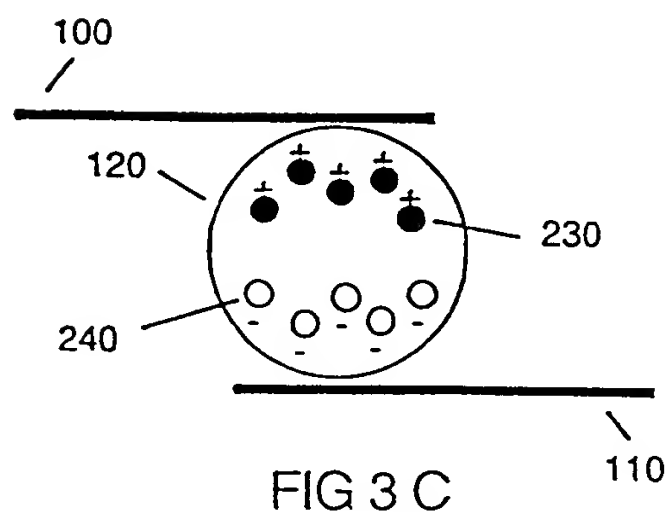
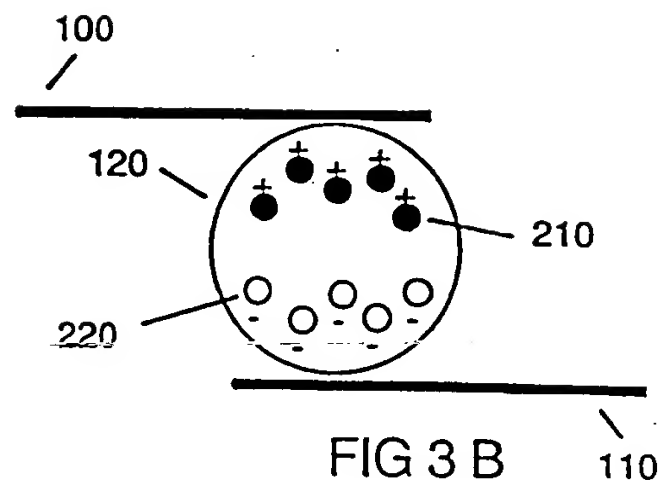
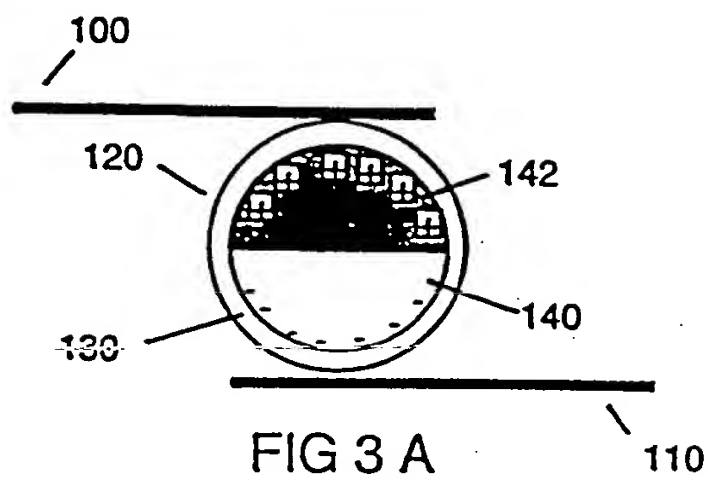


FIG 2 C



8/25



9/25

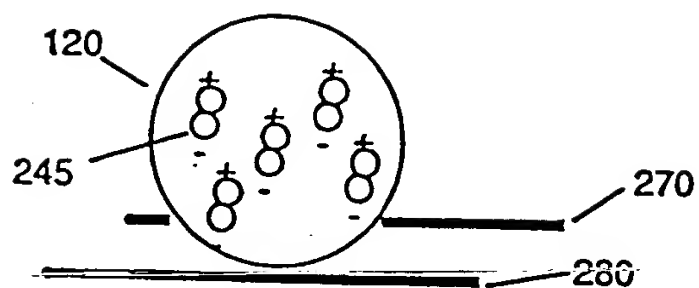


FIG 4 A

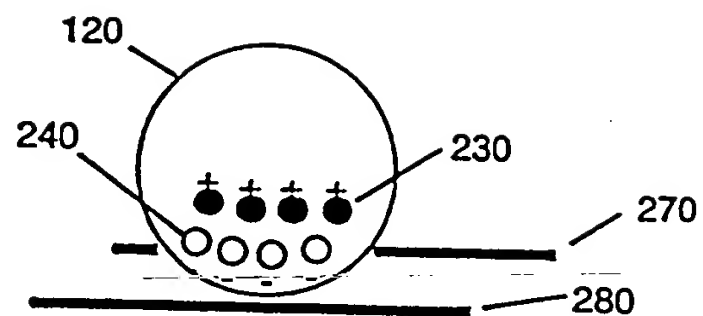


FIG 4 B

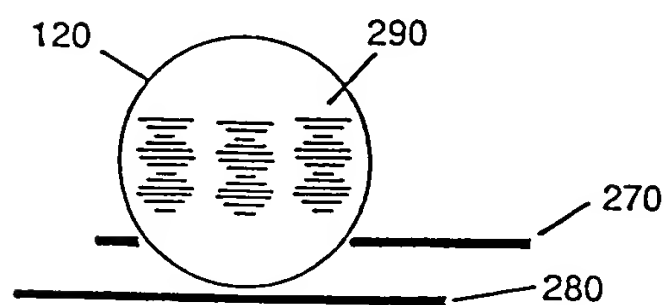


FIG 4 C

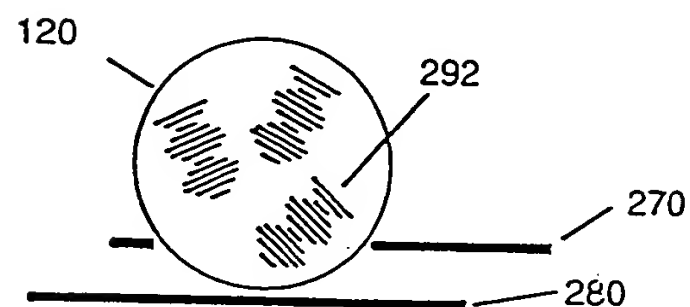


FIG 4 D

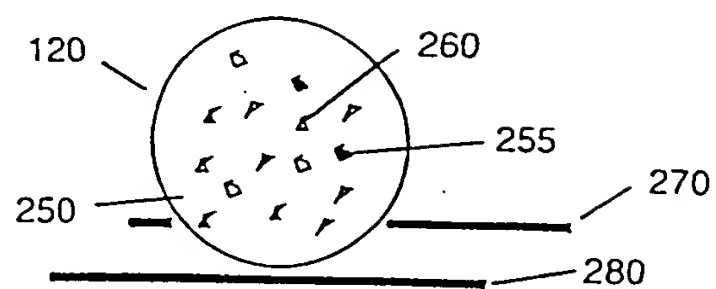


FIG 4 E

10/25

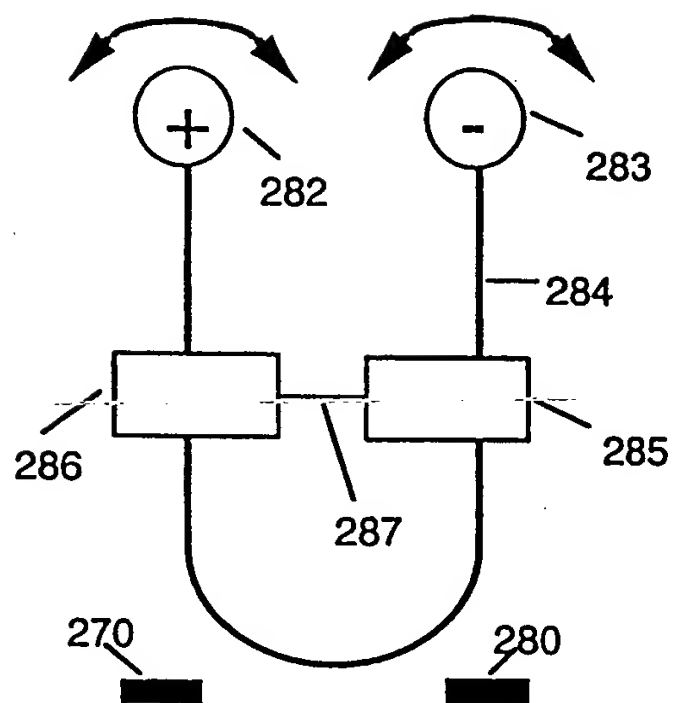


FIG 4 F

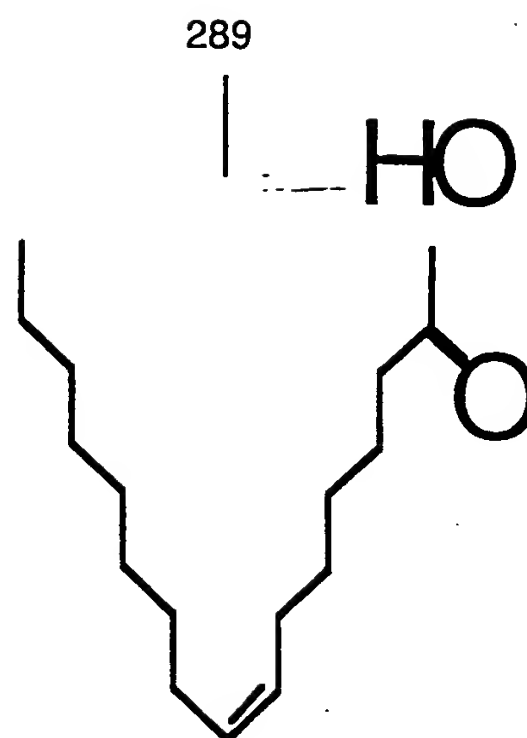


FIG 4 H

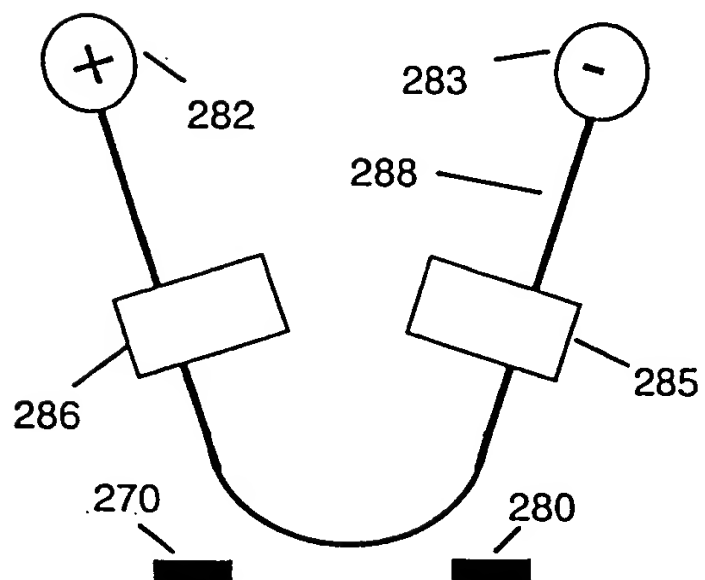


FIG 4 G

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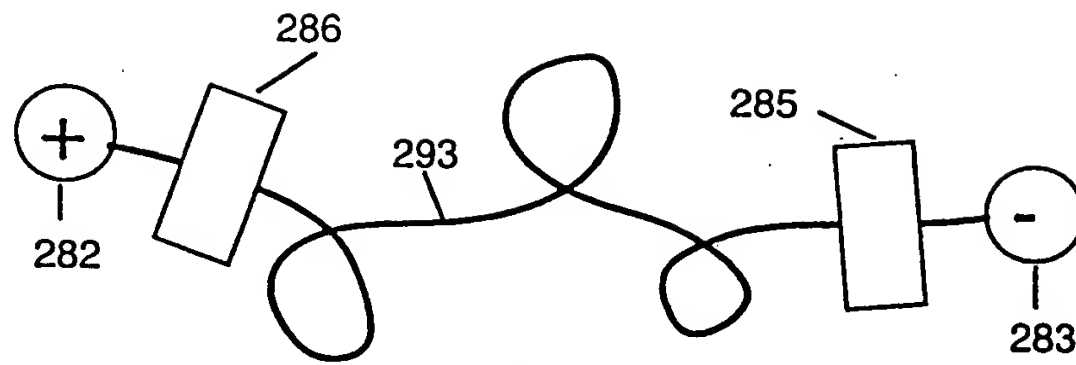


FIG 4 I

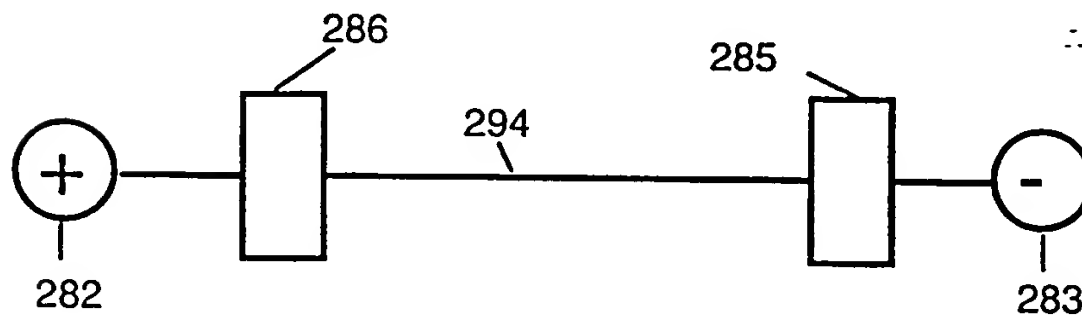


FIG 4 J

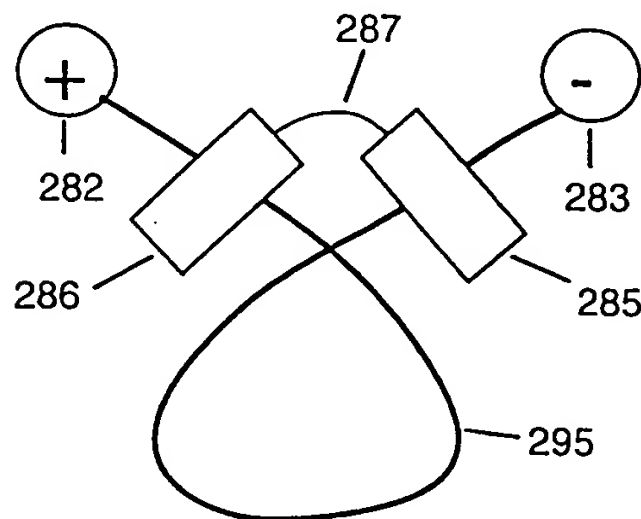


FIG 4 K

12/25

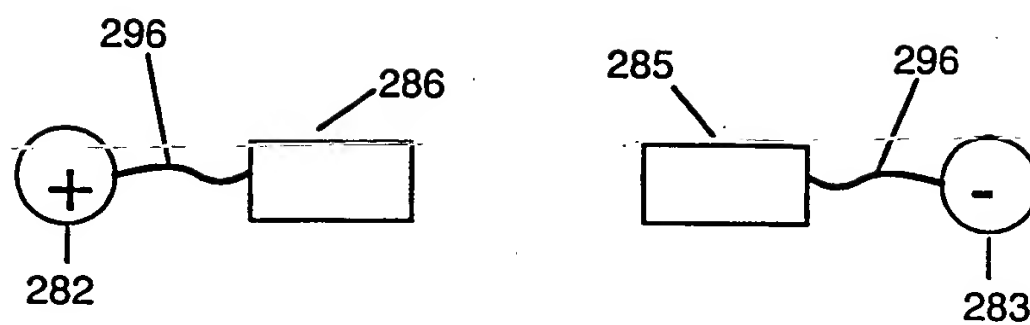


FIG 4 L

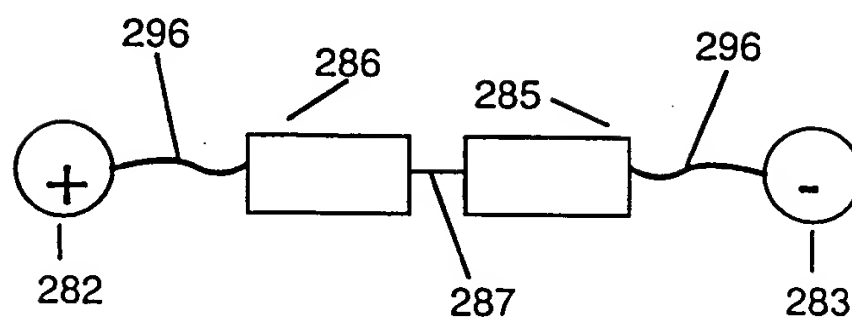


FIG 4 M

13/25

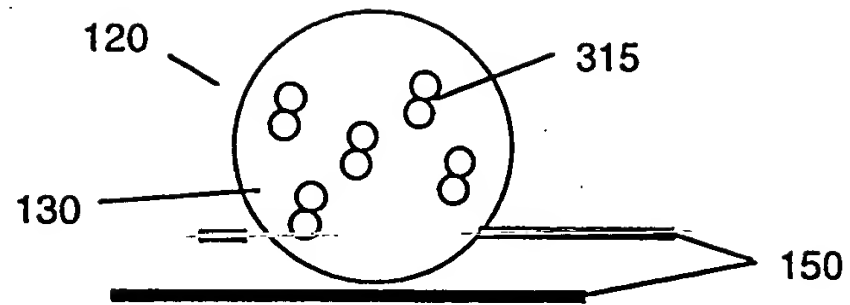


FIG 5 A

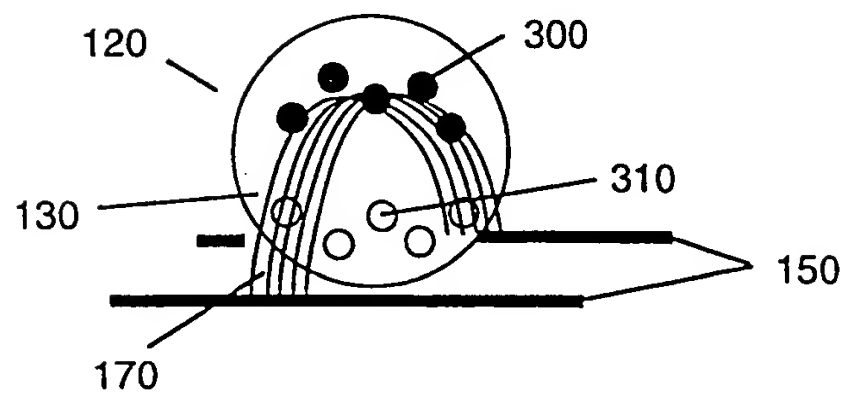


FIG 5 B

14/25

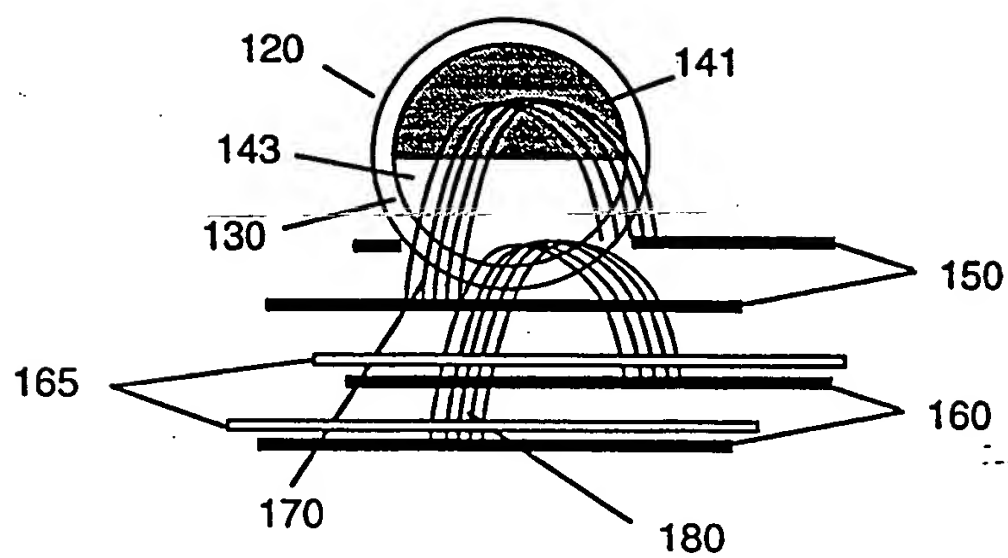


FIG 5 C

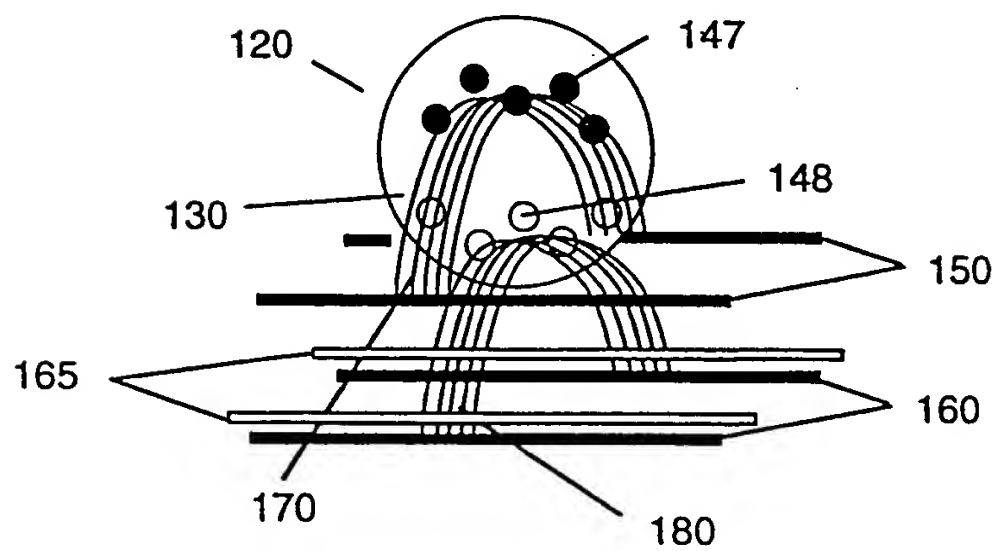


FIG 5 D

15/25

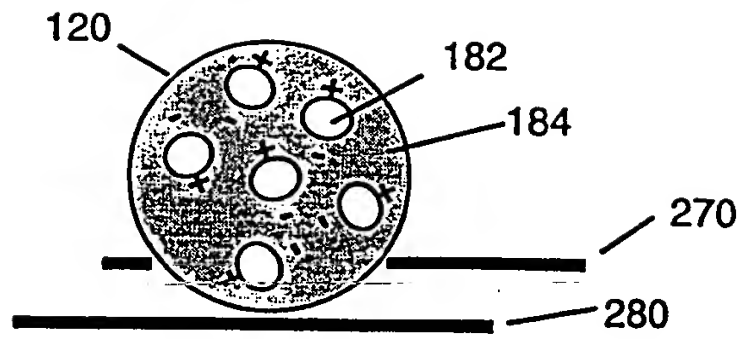


FIG 6 A

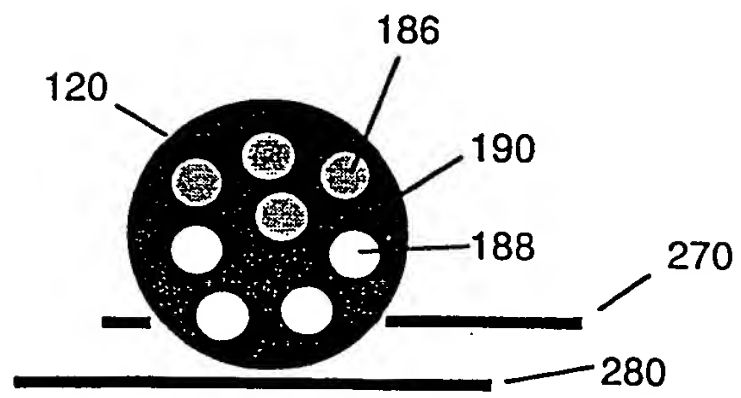
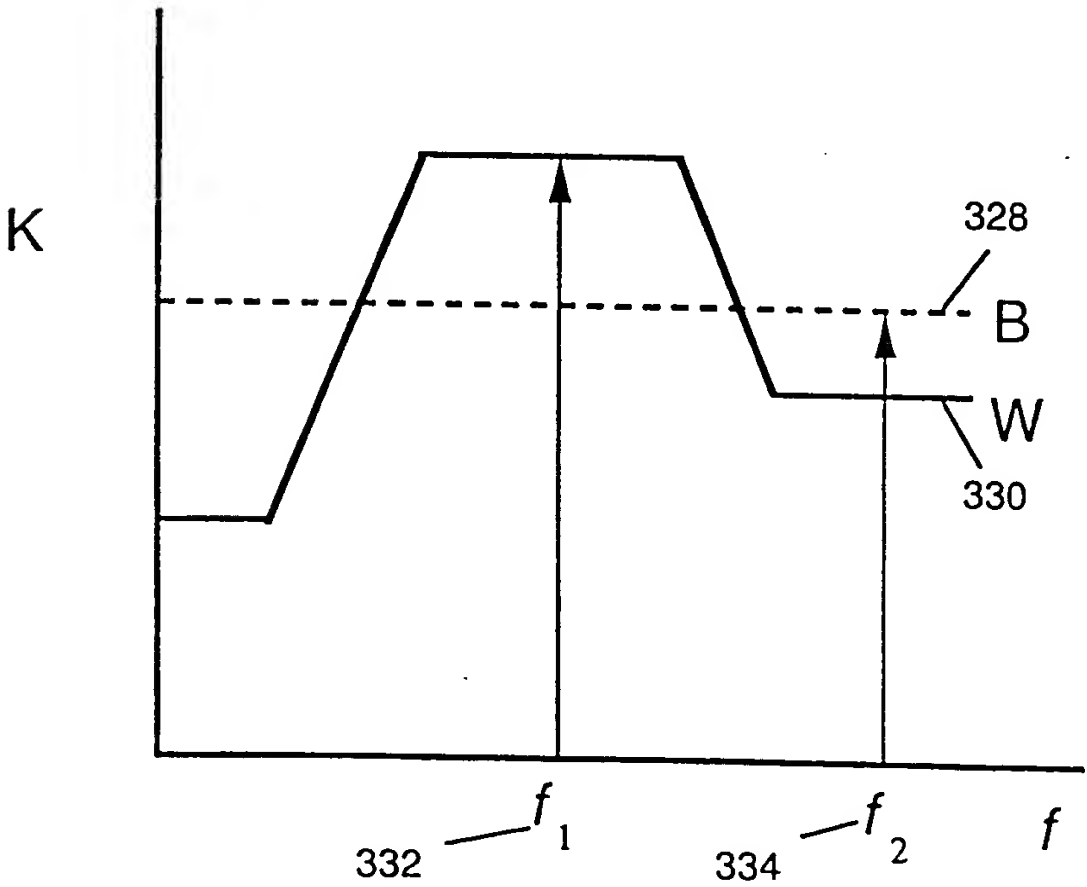
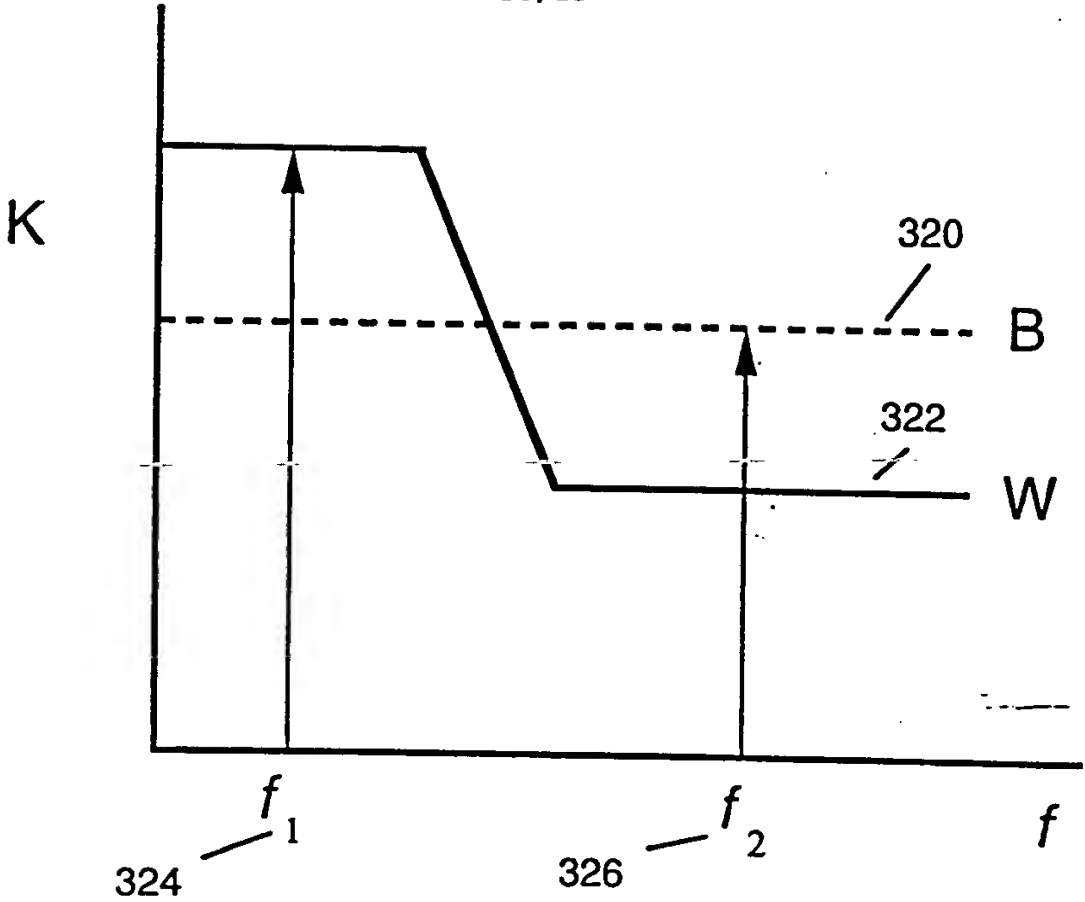


FIG 6 B



16/25



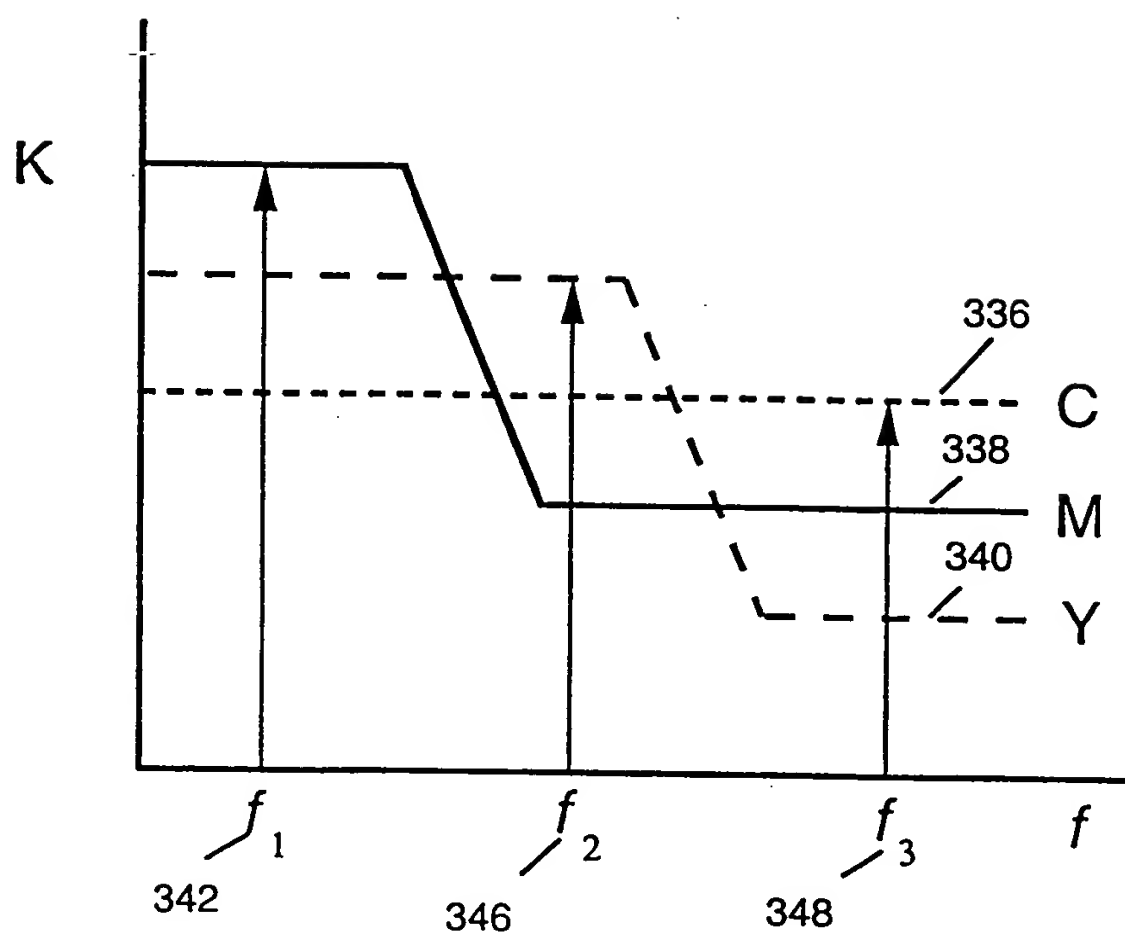


FIG 6 E

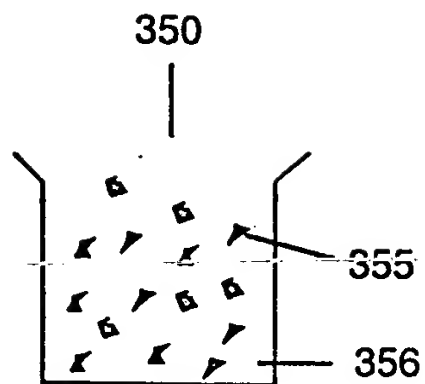


FIG 7 A

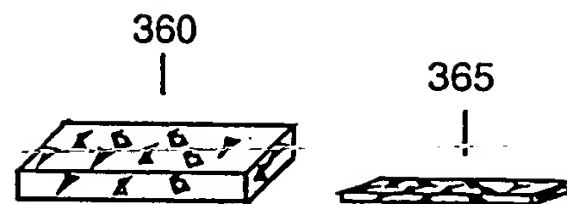


FIG 7 D

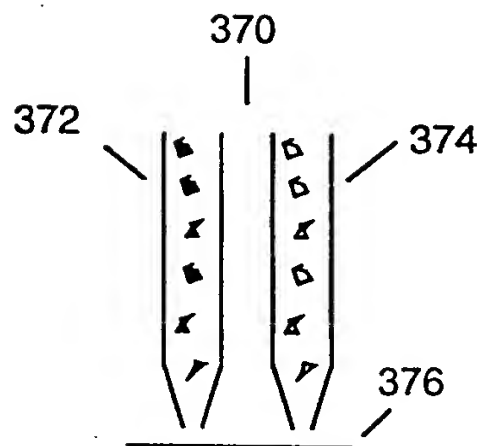


FIG 7 B

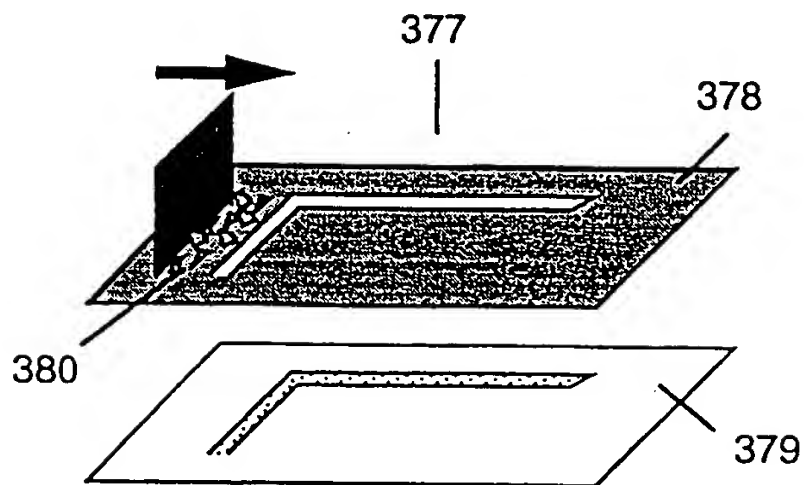


FIG 7 C

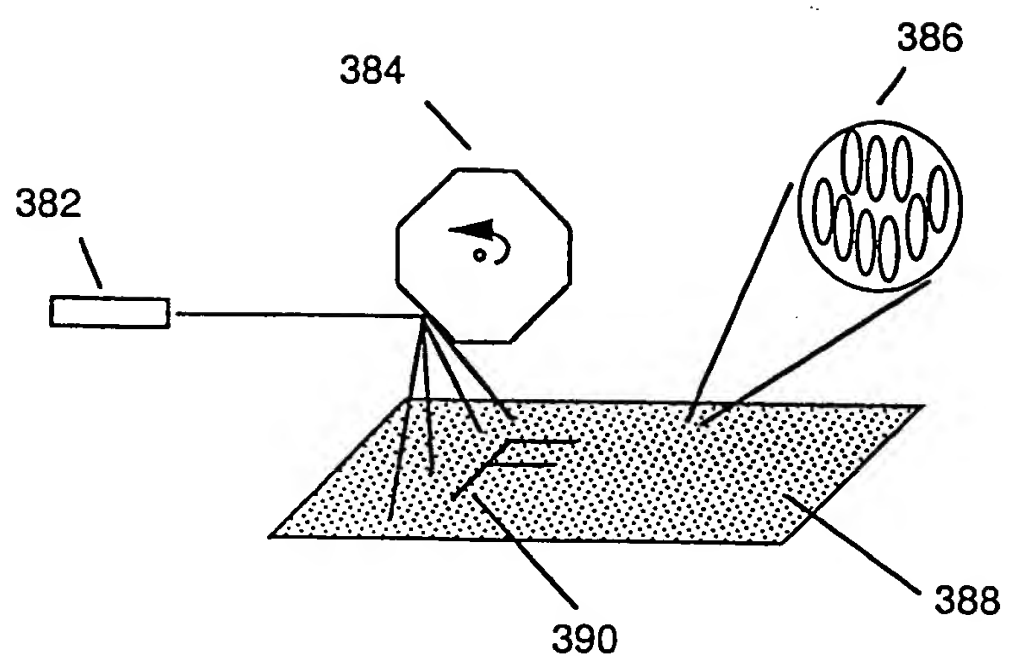


FIG 8

20/25

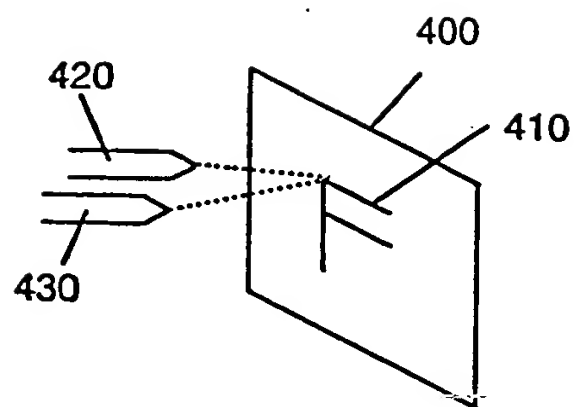


FIG 9 A

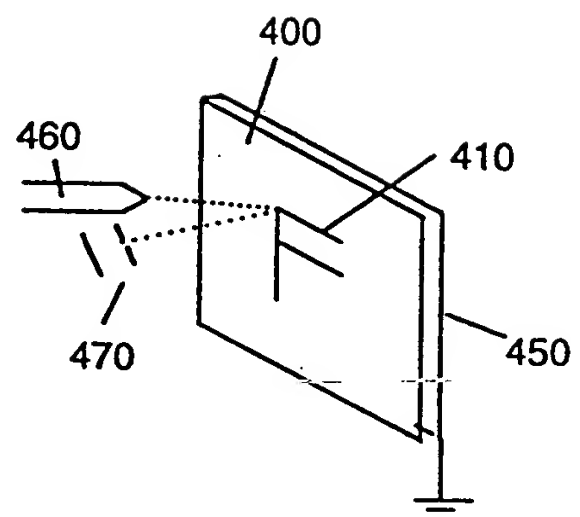


FIG 9 B

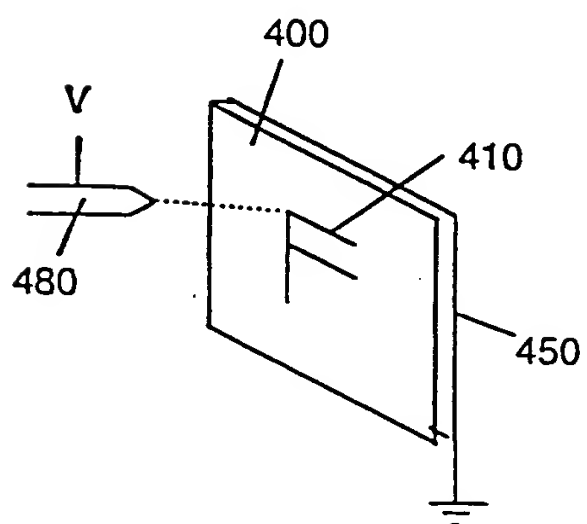


FIG 9 C

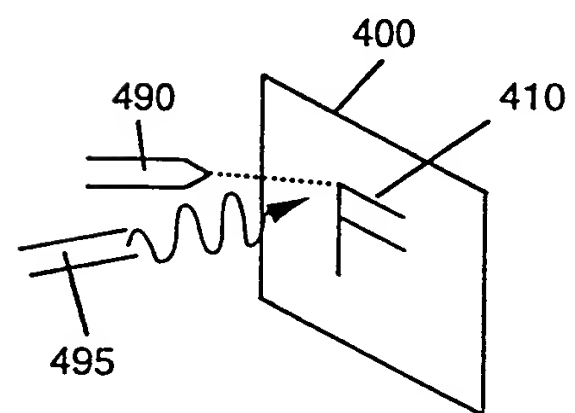


FIG 9 D

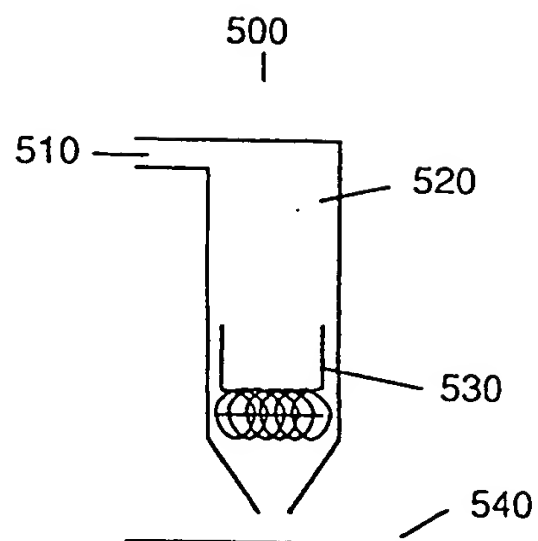


FIG 9 E

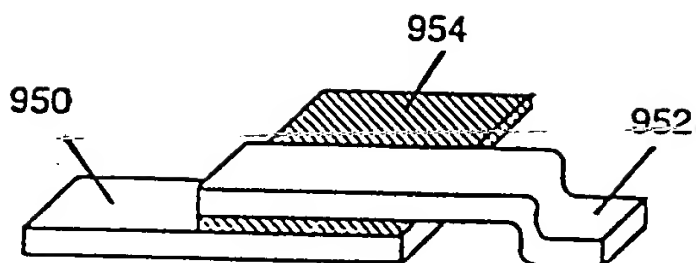


FIG 10 A

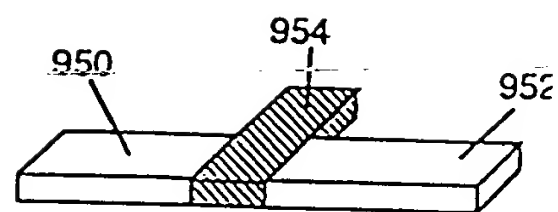


FIG 10 B

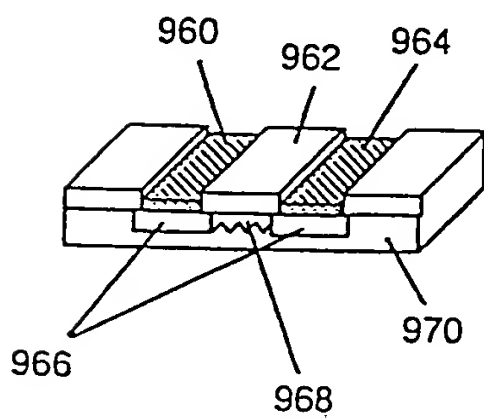


FIG 10 C

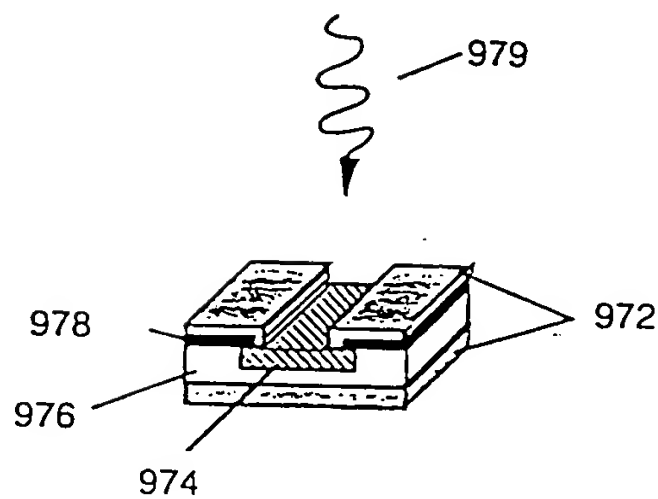


FIG 10 D

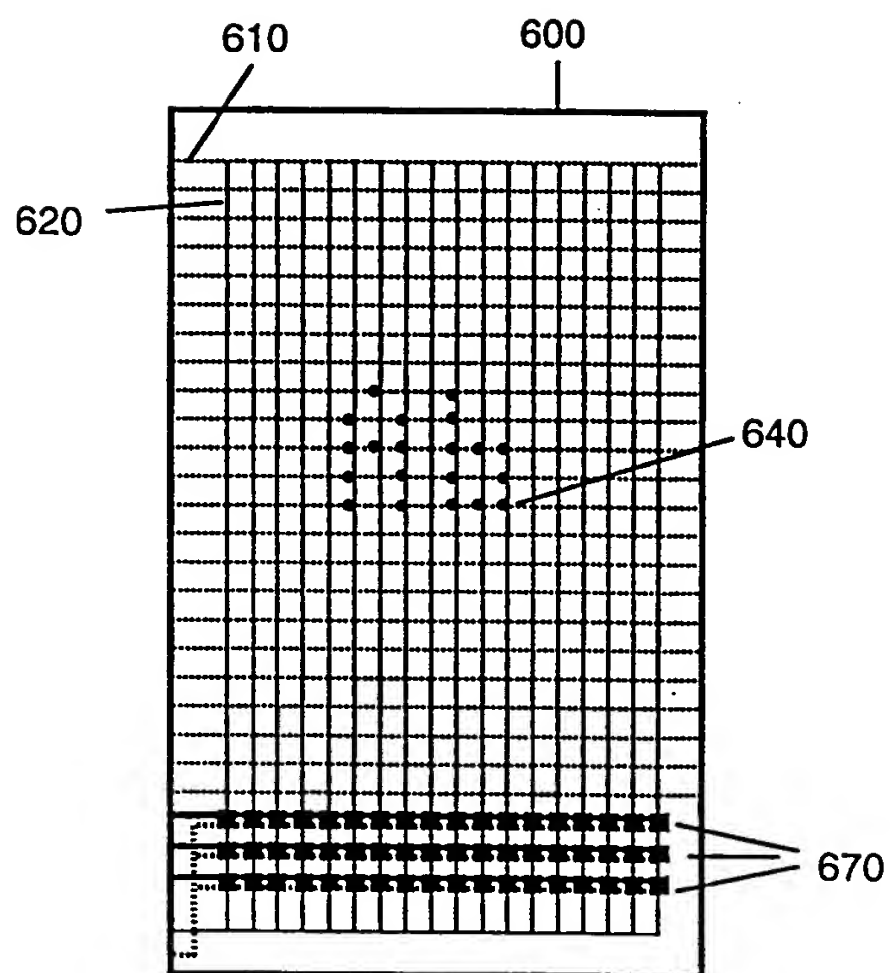


FIG 11

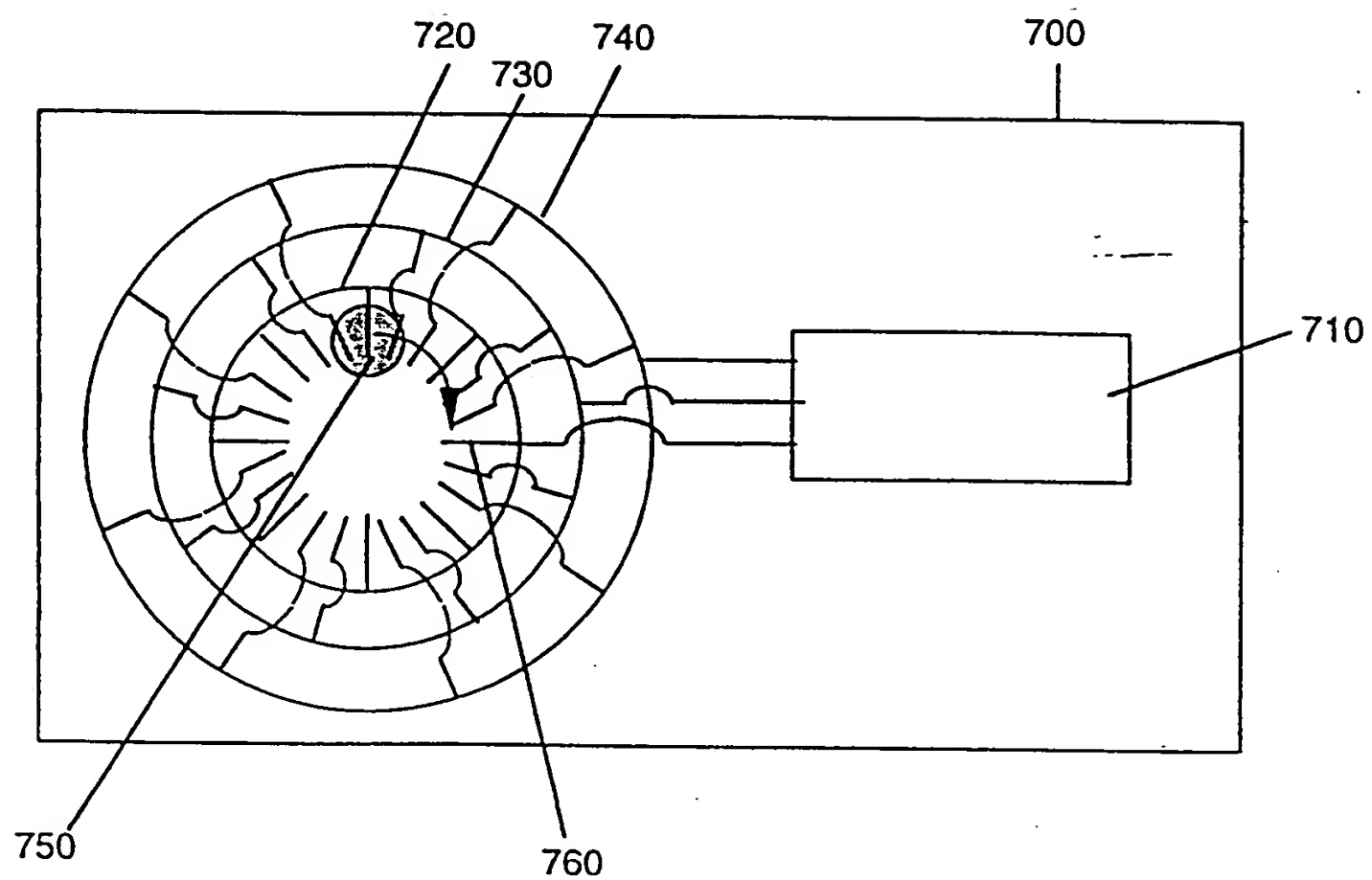


FIG 12



24/25

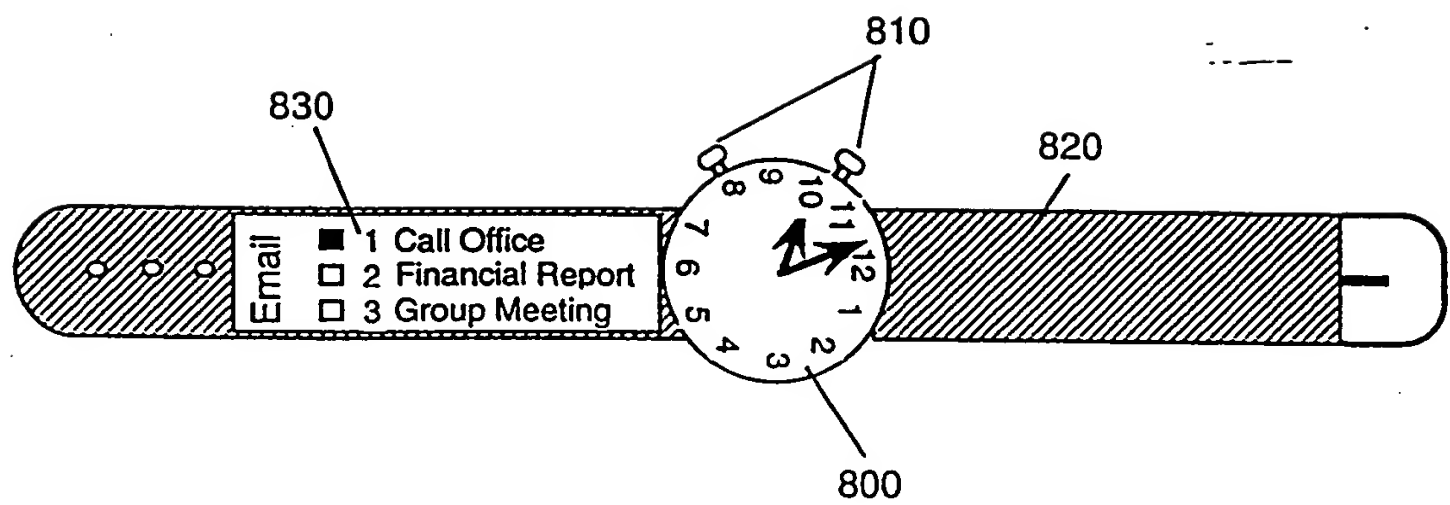


FIG 13

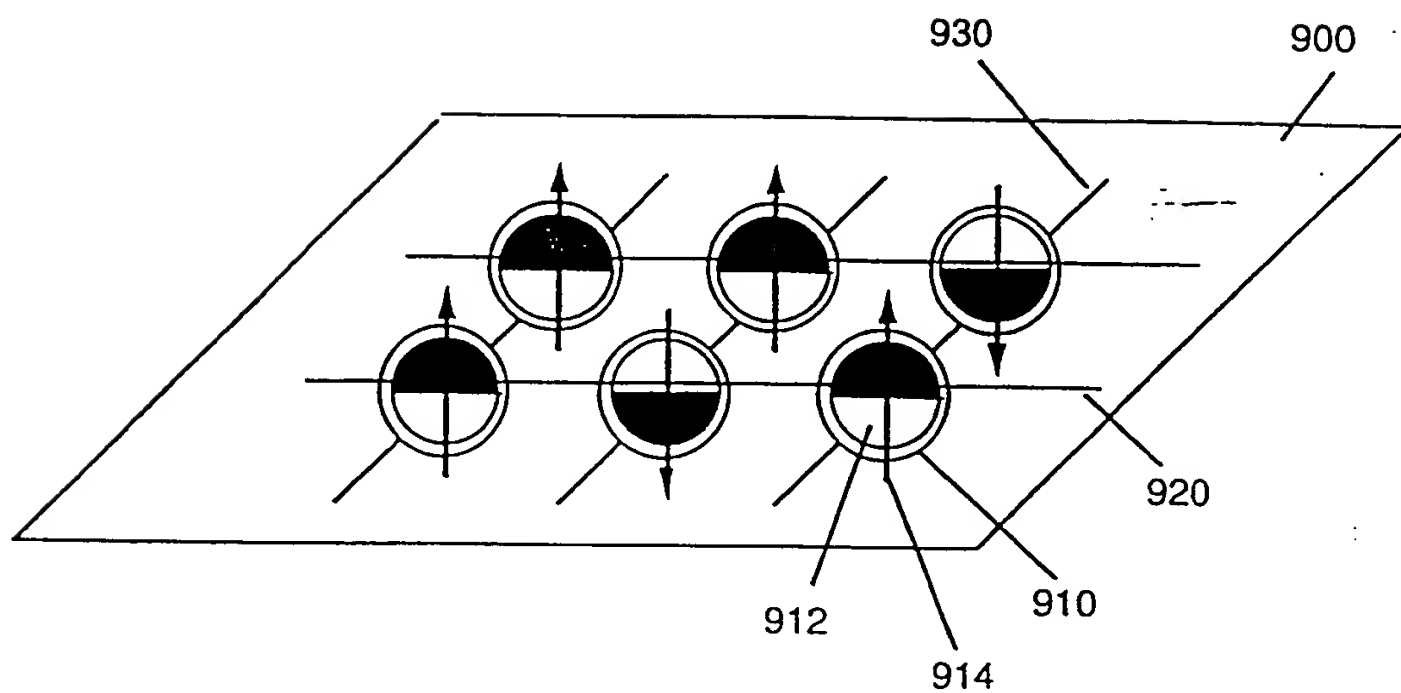


FIG 14